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Particle aggregation in gravity thickening

Roger Vaughn Stephenson
Iowa State University

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PARTICLE AGGREGATION IN GRAVITY THICKENING

Iowa State University

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Particle aggregation in gravity thickening

by

Roger Vaughn Stephenson

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Ames, Iowa

1985

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DEDICATION

To my wife, Kathleen

NOMENCLATURE AND ABBREVIATIONS

Nomenclature

A	aggregate diameter-density proportionality constant
A_p	particle surface area
a	empirical constant
C	solids concentration
C_D	drag coefficient
d_a	aggregate diameter
d_{app}	apparent primary particle diameter
d_p	primary particle diameter
g	gravitational acceleration
H	interface height
K	ratio of aggregate volume concentration to solids concentration
m	empirical constant
n	velocity-voidage correlation exponent
P/DA	polyelectrolyte dosage
Re	Reynolds number
t	time
V	hindered settling velocity
V_i	intercept velocity
V_o	unhindered settling velocity
v_p	particle volume
w	weight-percent solids concentration
x	aggregate diameter-density exponent
α	velocity-concentration proportionality constant

β	velocity-concentration exponent
γ	empirical constant
ϵ	porosity
η	intraaggregate void ratio
ζ	zeta potential
μ	dynamic viscosity
ρ_a	aggregate density
ρ_l	liquid density
ρ_p	primary particle density
ρ_s	solid density
τ_{\max}	maximum surface shear stress
τ_y	aggregate surface yield stress
ϕ_a	aggregate volume concentration
ϕ_{\max}	maximum aggregate volume concentration
ϕ_s	solids volume concentration

Abbreviations

cm	centimeter
ft	feet
g	gram
in	inch
kg	kilogram
ℓ	liter
lb _f	pound-force
m	meter
min	minute

x

ml	milliliter
mm	millimeter
mV	millivolt
rpm	revolutions per minute
sec	second
W	watt
μ m	micrometer

INTRODUCTION

Gravity thickening is a widely used solid-liquid separation process that has found application as a method of separating concentrated solids from process streams. It is used, for example, in the activated sludge process and in mineral processing operations, and as a method of reducing waste sludge volume prior to additional dewatering or ultimate disposal of the waste solids.

In gravity thickening, solids fed to a thickener settle and are concentrated under the influence of gravity, the concentrated solids are then withdrawn as the underflow from the bottom of the thickener while the clarified liquid constitutes the thickener overflow. As a sedimentation process, gravity thickening is distinguished from clarification in that, at the solids concentrations normally involved in gravity thickening, hydrodynamic and physical particle interactions occur which tend to resist the gravitational driving force. As a result, the effects of the solids concentration on settling, in addition to a consideration of the achievable underflow solids concentration, must be accounted for in the analysis and design of gravity thickeners.

Gravity Thickener Analysis and Design

The design and analysis of continuous-flow gravity thickeners with respect to solids loading capacity is generally based on the concepts of solids flux theory first presented by Coe and Clevenger (1917). Briefly, the solids flux theory states that the rate of downward movement of solids in a thickener per unit area, or flux, consists of two components--

the settling or gravitational flux and the bulk flux due to the withdrawal of thickened solids from the bottom of the thickener. For a given underflow concentration and withdrawal rate, a minimum net flux will exist which governs the maximum rate per unit area at which solids can be fed to the thickener and removed in the underflow. Yoshioka et al. (1957) are generally credited with expanding upon the solids flux theory and presenting a graphical method for analysis and design, while Keinath et al. (1976) extended the concepts further to a detailed analysis of continuous-flow thickener operation.

For suspensions or sludges which form compressible sediments at concentrations that are expected to occur within the thickener, consideration must also be given to the effect of the depth of the solids undergoing compression.

A variety of design procedures have been presented which necessarily rely on the conduct of laboratory-scale batch settling tests, pilot-scale continuous-flow thickener operation, and/or experience for the prediction of the solids loading capacity and degree of thickening that can be realized. For example, the settling velocity versus solids concentration data required for solids flux analysis can be obtained from a series of quiescent, batch-settling tests (using two-liter cylinders) conducted at the concentrations of interest for which the rate of interface subsidence is equal to the settling velocity. This procedure, as originally proposed by Coe and Clevenger (1917), is still used in design practice even though the settling velocities determined using such small cylinders are now known to be subject to batch test column height and diameter

effects (Dick and Ewing, 1967; Michaels and Bolger, 1962; Vesilind, 1968a). Gentle stirring during batch settling has been advocated as a method of producing more reliable results (Dick, 1972; Scott, 1970; Vesilind, 1979).

An alternate method for obtaining the necessary solids flux data for design was proposed by Talmage and Fitch (1955). Based on the theoretical analysis of Kynch (1952), a procedure was developed with which settling velocity data could be obtained for a range of solids concentrations from a single batch settling test. This procedure was favorably received because of its simplicity and, as with the method of Coe and Clevenger, the Talmage and Fitch procedure is the basis of some currently recommended design methods, although it is not recommended for use with most suspensions encountered in practice (Fitch, 1975b, 1979).

The estimation of thickener depth requirements and prediction of underflow concentrations when a zone of solids undergoing compression is expected within the thickener have similarly been the subject of a variety of theoretical and experimental approaches.

Need for Research

The controlling factor which governs the ability to thicken a suspension to the desired concentration with economical thickener area and depth, and which indirectly governs the success or failure of the various design methods that have been proposed, is the flocculent nature of the suspension. Fitch (1962) classified and described sedimentation as a function of the suspension concentration and the flocculent nature of the particles. Suspensions of nonflocculent particles settle

discretely at low concentrations, undergo hydrodynamically-hindered settling at intermediate concentrations, and form sediments which are noncompressible at the low solids pressures that are encountered in gravity thickening. Flocculent suspensions settle as discrete floc at low concentrations and undergo hydrodynamically hindered settling at intermediate concentrations. As a result of particle-particle attachments, structural integrity can exist throughout a flocculent suspension at higher concentrations which, in turn, can result in channelling, batch test column height and diameter effects, and the formation of compressible sediments.

Although batch and continuous-flow gravity thickening have been examined extensively in the literature, there have been relatively few investigations on the effects of the degree or magnitude of the flocculent nature of a suspension on its thickening behavior. Flocculated kaolinite has been used by many workers to investigate the rheological, batch and continuous-flow thickening, and sediment formation characteristics of a suspension as a function of its flocculent nature (Khatib and Howell, 1979; Melton and Rand, 1977a,b; Michaels and Bolger, 1962). By varying the conditions of electrolyte concentration and pH, the degree of flocculation of an aqueous kaolinite suspension can be varied. However, the differing degrees of flocculation that can be achieved with an aqueous kaolinite system are in part a result of the various configurations of the plate-like clay particles that can occur and therefore the direct comparison of such suspensions is not possible.

Investigations to be discussed later have also been conducted on the

effects of various degrees, or levels, of coagulation as controlled by suspension pH, coagulant dosage or coagulant type for a variety of particulate systems. These investigations were, however, limited by the ranges of suspension concentration or flocculent nature that were examined.

Such investigations and others have, however, identified the role of aggregate formation during thickening as one of major importance. Michaels and Bolger (1962) found that the settling units of a flocculated suspension were aggregates, or flocs, of the individual particles and that the hindered settling velocity of a flocculent kaolinite suspension was a function of the size, density, and concentration of the aggregates. The behavior of flocculent suspensions at higher concentrations in batch and continuous thickening has been conceptually modeled by considering the association of aggregates and their splitting and compaction (Harris et al., 1975; Javaheri and Dick, 1969; Michaels and Bolger, 1962; Scott, 1968a) and estimation of aggregate property changes during batch thickening have been made (Javaheri and Dick, 1969; Shin and Dick, 1975, 1980).

The physical and chemical variables that account for the flocculent nature of a suspension are, therefore, the variables that affect particle coagulation and flocculation: primary particle size, shape, and density, the nature of the interparticle bonding, the magnitude of the repulsive forces tending to prevent particle aggregation, and the prevailing--and possibly preceding--hydrodynamic conditions.

As a pretreatment operation prior to thickening, mixing or agitation

is required to obtain a uniform distribution of solids in a batch test and dispersion of coagulating agents in batch tests and continuous-flow thickeners. The existing experimental evidence on pretreatment mixing effects on thickening is conflicting. Intense agitation of flocculated kaolinite suspensions has been reported to increase the hindered settling velocity (Michaels and Bolger (1962), Khatib and Howell (1979)). Bodman et al. (1972) found no effect of mixing intensity on the settling rates of titanium dioxide suspensions. Pearse (1980) found that the settling rate of polyelectrolyte flocculated kaolinite decreased with increasing duration of gentle mixing. Warden (1981) found that thickener capacity and underflow concentration increased with mixing intensity for a surface water treatment sludge conditioned with a polyelectrolyte.

In order to gain a better understanding of the behavior of flocculent suspensions in gravity thickening, and of the reasons for the successes and failures of the various design methods, experimental and theoretical studies of the effects of the variables of coagulation and flocculation of particulate systems on the overall thickening behavior need to be conducted. Specifically, the effects of these variables on the formation of aggregates, as related to the thickening process, need to be examined as a first step in achieving a comprehensive delineation of the phenomena of batch and continuous-flow thickening of flocculent suspensions.

PURPOSE AND OBJECTIVES

The experimental investigation reported herein was conducted as part of a comprehensive investigation on the effects of particle surface potential and pretreatment mixing on batch and continuous flow thickening.¹ As previously noted, there has been a lack of systematic investigations on the effects of the variables of flocculent nature on batch thickening, sediment characteristics, and continuous thickening. The investigation was undertaken, therefore, to examine and compare the effects of a range of surface potentials and mixing conditions on the batch and continuous-flow thickening behavior of a suspension.

The experimental work was limited in scope to an examination of the batch settling and thickening behavior of laboratory prepared, polyelectrolyte-coated suspensions of known and controllable surface potential.

The specific objectives of this study were to:

1. Determine the effects of particle surface potential, as governed by the polyelectrolyte dosage, on the batch settling velocity of the suspension for a wide range of suspension concentrations,
2. Determine the effect of pretreatment mixing intensity on the batch settling velocity of the suspension, and

¹"Surface potential and mixing effects in gravity thickening," C. S. Oulman, Principal Investigator, United States Environmental Protection Agency, contract no. RB11710-01-0

3. Quantify, through the use of settling velocity correlations, the observed batch settling behavior as a function of the characteristics of the aggregates which form during the batch settling process.

REVIEW OF LITERATURE

Flocculent Nature of Particulate Systems

The flocculent nature of a system of particulates suspended in a fluid can be defined as the tendency for the formation of particle-particle attachments or bonding of a physical-chemical nature when the particles are brought into contact. The formation of such attachments results in aggregation or flocculation of the particles in relatively dilute suspensions and the formation of networks of inter-connected particles at higher concentrations. With respect to thickening, the tendency of a suspension to flocculate causes a variety of phenomena including channelling and the formation of compressible sediments as discussed by Fitch (1962). The sediments of flocculent systems are of relatively low bulk density and exhibit psuedo-plastic rheological behavior (van Olphen, 1977; Melton and Rand, 1977a,b). The flocculent nature of a system of particulates is a function of the degree of the tendency for particle attachment and the nature of the attachments. The resulting suspension behavior is conditional upon the size and shape of the particles, and the existence of hydrodynamic and mechanical forces acting on the system.

Particle attachment mechanisms

Inorganic particulates in water generally possess a net electrical charge because of imperfections in the crystal lattice, the presence of potential determining ions, or the adsorption of peptizing ions. Counter ions of opposite charge will accumulate in the liquid

surrounding the particle in order to balance the net charge of the particle. The result is an electrical potential difference between the bulk of the solution and the particle surface. The magnitude of this potential difference is a function of the surface charge of the particle and the ionic strength of the solution and, when sufficiently large, the potential difference acts as a barrier preventing the close approach of like particles and aggregation or flocculation is lessened or does not occur.

The zeta potential is defined as the potential difference between the bulk of the solution and the shear plane which is the boundary of an immobile layer of water which is associated with a particle. Though not equal to the surface potential (slightly less in magnitude), the zeta potential is readily measured using electrophoretic techniques and is commonly used as an approximation of the surface potential.

A reduction of the magnitude of the energy barrier will allow like particles to come into the range of van der Waals attractive forces and bonding of the particles will occur resulting in the formation of aggregates or flocs. This can be achieved by changes in the solution chemistry, i.e., pH or electrolyte composition and strength, or by the adsorption of charge neutralizing species onto the surface of the particles.

Organic polyelectrolytes are frequently used as charge neutralizing species for inorganic particles. A variety of polymeric molecules are used with molecular weights (in grams per mole) ranging from tens of thousands up to several million. The charged nature of these molecules

arise from the presence of ionizable functional groups. As a result of the size of these organic polyelectrolytes, an additional mechanism of particle-particle attachment can occur--that of bridging--in which a single polyelectrolyte molecule will attach to more than one particle. Bridging does not require charge neutralization and negatively charged particles can be successfully flocculated with both nonionic and anionic polymers, as well as with cationic polymers.

Systems of organic particulates also possess surface charge characteristics and, depending on the prevailing conditions, can aggregate and flocculate. For example, activated sludge organisms can readily flocculate as a result of the presence of extracellular polymers. The presence of filamentous organisms can also contribute to the flocculent nature of a biological suspension resulting in a highly "flocculent" system which is difficult to dewater by gravity thickening.

Physical factors affecting flocculent nature

The physical-chemical conditions of a system of particulates can be such that particle attachment can occur, but there are several other conditions that must be met before the outward appearances of flocculent nature, such as aggregation or the formation of compressible sediments, exist.

In very dilute systems, the particles must be brought into contact by one of two transport mechanisms. The transport of particles by their random motion induced from thermal motion of the surrounding water molecules and resulting interparticle contact is termed perikinetic flocculation. The transport and contact of particles due to a

difference in their velocities can be the result of velocity gradients within the suspension (orthokinetic flocculation) or the result of differential sedimentation.

In systems of very high concentration, these mechanisms undoubtedly exist, but contact of particles may be insured solely by the number of particles and their resulting close proximity.

For the formation of aggregates or compressible sediments to occur, the attachment forces must be strong relative to those forces tending to disrupt the particle associations. This is primarily a function of particle size. As particle size increases, the attachment forces per unit area will decrease while the disruptive forces of gravitational acceleration and fluid drag will increase. Tiller and Khatib (1983) have suggested a rough size range of 10 to 50 μm that marks the transition from flocculent to nonflocculent suspension behavior.

Particle shape would also be a factor contributing to the flocculent nature of a suspension through the surface area per unit volume and through the effect of packing arrangement that could be achieved. A prime example of this would be the role of platelet structure in the properties of flocculated kaolinite suspensions (van Olphen, 1977).

The flocculent nature of a particulate system is therefore a complex function of a number of factors. Particle morphology (size and shape), the nature and strength of repulsive forces and interparticle attachments, and the nature and strength of disruptive forces all contribute to the behavior of a suspension which could be classified as

flocculent.

Batch Thickening of Nonflocculent Suspensions

Nonflocculent suspensions are those suspensions for which particle-particle attachments do not occur. The settling of concentrated nonflocculent suspensions is restricted, or hindered, by hydrodynamic particle interactions and by direct contact at high concentrations. Ideal suspensions are those nonflocculent suspensions that are characterized by spherical particles of uniform size and density. Though rarely encountered in practice, ideal suspensions are of interest from a theoretical point of view and ideal suspension behavior has served as the basis for much of the work that has been conducted on the settling and fluidization of particulate systems.

Ideal suspension thickening--Kynch theory

Kynch (1952) presented a theoretical analysis of the batch settling of an ideal suspension which was made possible by assuming an initially uniform concentration of particles and that the velocity of fall of any particle is a function of only the local concentration of particles.

The batch settling of an ideal suspension can be characterized by the suspension-supernatant interface position as a function of time as illustrated by Figure 1. The interface initially settles at some constant rate as governed by the initial suspension concentration. The rate of subsidence then decreases to zero as the particles accumulate as an incompressible sediment.

The main result of Kynch's analysis is an interpretation of the observed interface behavior. At the onset of settling, an infinitesimal

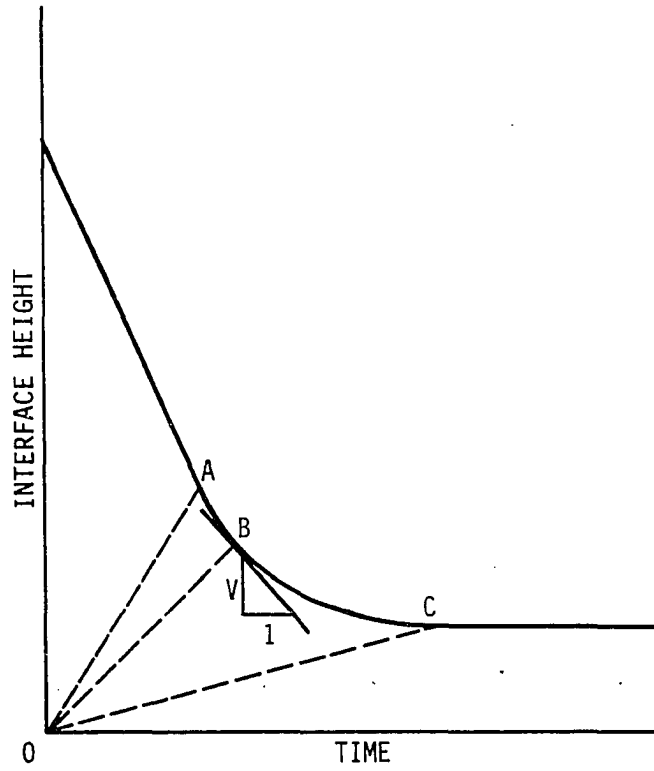


Figure 1. Interface height versus time for the batch thickening of an ideal suspension

layer of suspension is deposited on the bottom of the container at the maximum concentration. As the particles accumulate, this layer propagates upward at a constant, characteristic velocity and its appearance at the surface marks the end of the settling process and no further interface subsidence occurs (line \overline{OC} , Figure 1). Layers of all intermediate concentrations between the initial and maximum concentrations also form and propagate upward at characteristic velocities with the propagation velocity increasing with decreasing layer concentration (line \overline{OB} , Figure 1). As each layer of intermediate concentration reaches the interface, the interface subsides at a rate, V , corresponding to that particular concentration. The decreasing rate portion of an ideal interface subsidence curve, therefore, is a result of an increasing interface concentration.

Kynch's analysis was conducted without specifying a functional relationship between velocity and concentration. The existence of an interface subsidence curve with a declining rate period will, however, be controlled by the dependence of settling velocity on the solids concentration and the initial solids concentration, as discussed by Shannon et al. (1964), Shannon and Tory (1965), and Shin and Dick (1980). For example, as verified by Shannon et al. (1964) using suspensions of glass spheres, both low and high initial concentrations can settle at a constant rate and then abruptly stop.

Talmage and Fitch (1955) added to Kynch's analysis by demonstrating a method of obtaining a range of concentration versus settling velocity data from a single batch settling test for use in thickener design.

This design method received a considerable amount of attention due to its simplicity and is the basis for some currently used design methods even though it is not generally applicable to real sludges and is not recommended by Fitch (1975b, 1979). Shin and Dick (1980) investigated the applicability of the Kynch theory to a calcium carbonate suspension which could be considered, at least, mildly flocculent. The observed interface behavior and concentration profiles were, however, in general agreement with predicted behavior based on ideal suspension theory.

Various workers have considered the method of Talmage and Fitch to be valid until a "compression point" is reached (Behn and Liebman, 1963; Eckenfelder and Melbinger, 1957). The effects of sediment compaction have been considered in recent theoretical and experimental extensions of the Kynch theory to suspensions which form compressible sediments (Tiller, 1981; Fitch, 1983; Dixon, 1982).

Hindered settling of nonflocculent suspensions

The terminal settling velocity of an individual particle in an infinite expanse of fluid is a function of the size, shape, and density of the particle and of the fluid density and viscosity as given by:

$$V_o = \left\{ \left[\frac{2g(\rho_p - \rho_l)}{C_D \rho_l} \right] \left(\frac{v_p}{A_p} \right) \right\}^{1/2} \quad (1)$$

where V_o = terminal settling velocity, g = gravitational acceleration, ρ_p and ρ_l = particle and fluid densities, v_p = particle volume, A_p = particle surface area, and C_D = drag coefficient which is a function of the Reynolds number, $R_e = (V_o d_p \rho_l) / \mu$ where d_p = particle diameter and

μ = dynamic viscosity. For spherical particles experiencing creeping flow for which Re is less than 0.1, the drag coefficient is equal to $24/Re$ and Equation (1) becomes:

$$V_o = \frac{g}{18\mu} (\rho_p - \rho_l) d_p^2 \quad (2)$$

which is known as Stoke's Law.

The settling velocity of an assemblage of particles is less than that of the individual particles due to the number of particles present and, as a result, an interface forms between the settling particles and the overlying fluid. Four effects of concentration are considered to be of possible importance to hindered settling (Zimmels, 1983a). An increase in concentration results in:

1. a decrease in the cross-sectional area available for liquid flow,
2. an increase in suspension viscosity,
3. a restriction of flow patterns, and
4. a decrease in gravitational driving force due to an increase in suspension density.

Various combinations of these hinderance factors have been used to develop velocity-concentration (or voidage) relationships for hindered settling and fluidization. For example, Steinour (1944a) presented a semi-theoretical analysis of hindered settling of uniform spheres that was based on a model similar to the capillary-bundle model of fluid flow through a porous bed. The size and shape of the flow paths were assumed to be a function of suspension porosity, and the

increased suspension density due to concentration was incorporated into the model. The effect of porosity on the size and shape of the flow paths was determined experimentally. The correlation was found to be applicable to suspensions of angular particles provided that a correction term, which was believed to represent an amount of immobile fluid that was associated with each particle, was subtracted from the suspension porosity (Steinour, 1944b).

Happel (1958) presented a theoretical velocity-voidage relationship that was based on the solution of mass and momentum balance equations for a settling sphere that was surrounded by an envelope of fluid.

Richardson and Zaki (1954) presented an empirical velocity-voidage relationship for settling and fluidization that was based on dimensional analysis of the variables of particle resistance, flow path size and shape, and, additionally, the settling test column diameter. This velocity correlation is of importance to this dissertation and will be examined in more detail later.

These velocity-voidage correlations, along with correlations obtained by other workers, have been compared by various authors including Shannon et al. (1963) and Garside and Al-Dibouni (1977) who presented additional empirical correlations. Though no two correlations are alike, the available correlations are in general agreement even though there appear to be conditions or concentration ranges for which a particular correlation may be preferable.

More recently, theoretical velocity-voidage relationships have been presented that consider both non-steady and steady-state flow regimes

(Zimmels, 1983a), the influence of long range interparticle electrostatic repulsive forces (Reed and Anderson, 1983), and mixtures of nonuniform particle size and density (Zimmels, 1983b). Also, particle shape has been found to be an important variable of fluidization and was incorporated into a velocity-voidage correlation by Dharmavajah (1982).

Richardson and Zaki correlation

Richardson and Zaki (1954) used dimensional analysis and their own experimental data and the data of others to obtain a velocity-voidage relationship for the hindered settling and fluidization of spherical particles. The terminal settling velocity of a single spherical particle was assumed to be a function of the fluid density and viscosity, the particle diameter and density, and the resistance force per unit area of the particle. The diameter of the settling column was also assumed to be of importance due to the possible interference of the column wall when in close proximity to a settling particle. The hindered settling velocity relative to the container wall was also assumed to be a function of the porosity of the suspension because of the effect of concentration on the size and shape of the flow paths and because porosity is the proportionality constant that relates the particle velocity relative to the fluid to the velocity relative to the wall of the container.

The resistance force per unit particle area was shown to be a function of the Reynolds number and, therefore, four dimensionless groups were required which resulted in:

$$\frac{V}{V_o} = f(Re, d_p/D, \epsilon) \quad (3)$$

where V = hindered settling velocity, d_p/D = ratio of particle diameter, d_p , to column diameter, D , and ϵ = suspension porosity.

For given values of Re and d_p/D , the experimental data fit an equation of the form

$$\log V = n \log \epsilon + \log V_i, \text{ or} \quad (4)$$

$$V/V_i = \epsilon^n \quad (5)$$

where n = slope and V_i = intercept velocity.

Any deviation of the intercept velocity from V_o was assumed to be an effect of the particle to column diameter ratio. Hence,

$$\frac{V}{V_i} = \epsilon^n = f\left(\frac{V}{V_o}, d_p/D\right) = f(Re, \epsilon, d_p/D) \quad (6)$$

and therefore,

$$n = f(Re, d_p/D) \quad (7)$$

Based on sedimentation and fluidization data covering a wide range of conditions, the following correlations for n were proposed:

$$Re < 0.2 \quad n = 4.65 + 19.5 d_p/D \quad (8)$$

$$0.2 < Re < 1 \quad n = (4.35 + 17.5 d_p/D) Re^{-0.03} \quad (9)$$

$$1 < Re < 200 \quad n = (4.45 + 18 d_p/D) Re^{-0.1} \quad (10)$$

$$200 < Re < 500 \quad n = 4.45 Re^{-0.1} \quad (11)$$

$$500 < Re \quad n = 2.39 \quad (12)$$

Richardson and Zaki also noted that for the data from sedimentation

experiments, the intercept velocity equaled the calculated terminal settling velocity. For fluidization, the ratio of V_0/V_i was a function of d_p/D .

Garside and Al-Dibouni (1977) examined the Richardson and Zaki correlation with respect to the data that was at that time available in the literature. They proposed the following alternate expression for n that was based on a best-fit logistic curve for the full range of Reynolds numbers:

$$\frac{5.09 - n}{n - 2.73} = 0.104 \text{ Re}^{0.877} \quad (13)$$

The constants 5.09 and 2.73 represent the asymptotic values of n for creeping flow and fully turbulent flow, respectively. In their correlation, the terminal settling velocity of an individual particle, V_0 , is that velocity occurring in a test column. Relationships for correcting for the test column diameter were presented. They also noted that correlations of the type of Richardson and Zaki were not considered by others to adequately represent systems for which $\epsilon > 0.9$, which would result in an overestimation of the terminal settling velocity, V_0 .

Selim et al. (1983) applied the modified Richardson and Zaki correlation, Equation (13), to the sedimentation of multisized suspensions of spherical particles.

Richardson and Jerónimo (1979) demonstrated that for intermediate Reynolds numbers and small values of d_p/D , n can be calculated from the slope of a log-log plot of friction factor versus Reynolds number for an isolated spherical particle. The asymptotic values of n were found to

be 4.6 for $Re < 0.2$ and 2.3 for $Re > 500$.

Other workers have investigated the effects of particle shape on the exponent of Equation (5). Chong et al. (1979) found that for creeping flow, n varied from 4.8 for spheres to 5.8 for angular particles. Their results were reflected by a plot of n versus settled bed porosity. Cleasby and Fan (1981) found that for fluidization at transitional Reynolds numbers, measured values of n could be correlated by either the dynamic shape factor or the sphericity of the particles.

Batch Thickening of Flocculent Suspensions

The batch thickening of flocculent suspensions is characterized by a variety of phenomena which occur as a result of the flocculent nature of the particles and the relative suspension concentration. These phenomena include hindered settling as an assemblage of aggregates or floc and a dependence of the batch settling characteristics on the test column dimensions. In some instances, the batch settling behavior of a flocculent suspension is readily interpreted in terms of the concepts and velocity-voidage correlations that have been developed for nonflocculent suspension behavior. Much of the documented flocculent suspension behavior, however, has been beyond rigorous analysis because of the number of variables and variety of phenomena that are involved.

Concentration dependent thickening behavior

Michaels and Bolger (1962) classified the unstirred, batch-thickening behavior of flocculent kaolinite suspensions according to concentration ranges as illustrated by Figure 2. For relatively dilute

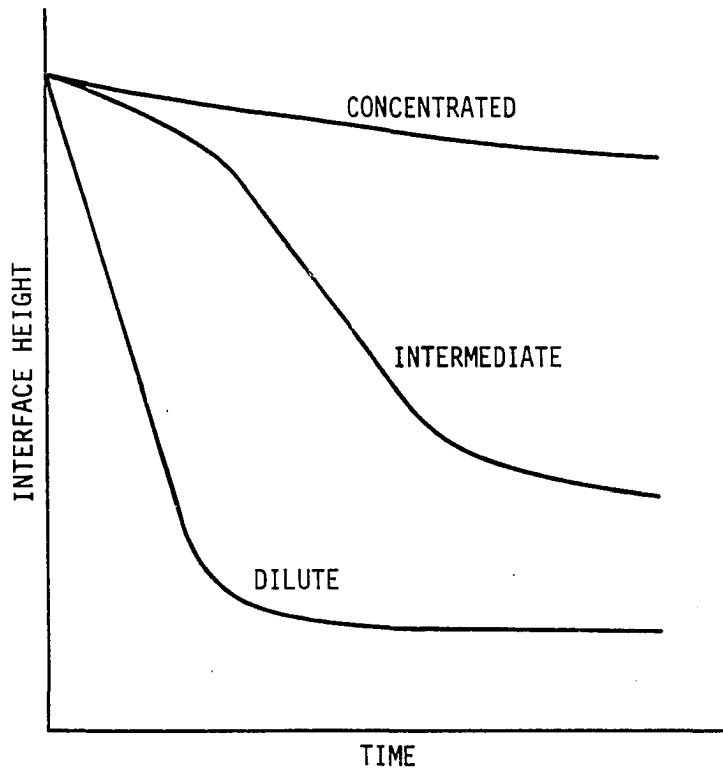


Figure 2. Typical interface height versus time for unstirred, batch thickening of dilute, intermediate, and concentrated flocculent suspensions (after Michaels and Bolger, 1962)

initial concentrations, the solid-liquid interface subsided at a constant rate for an extended distance followed by a rapid decrease in velocity as the sediment formed on the bottom of the column.

Suspensions of intermediate concentration underwent an initial period of interface acceleration to some maximum subsidence velocity. The period of acceleration was believed to represent the gradual formation of a structural network within the suspension and channels of low hydraulic resistance. Concentrated suspensions settled at an ever decreasing rate and were considered to be in compression.

Dilute suspensions The constant rate of interface subsidence that commences immediately upon the initiation of batch settling is characteristic of true hindered settling. Michaels and Bolger (1962) observed that aggregates, or flocs, were the primary settling units for this concentration range. Because dilute flocculent suspensions settle as individual aggregates without interaggregate attachment, the settling velocities are not affected by gentle stirring using picket rake mechanisms, nor are the velocities a function of initial suspension height. A column diameter effect can, however, occur (Vesilind, 1968a; Dick and Ewing, 1967). An increase in settling velocity with decreasing column diameter may occur due to an increase in the ratio of flow of fluid, displaced from below, along the smooth column wall to the upward flow through the suspension.

An induction period required for the formation of aggregates has been considered as a general characteristic of flocculent settling (Coe and Clevenger, 1917; Gaudin et al., 1959; Vesilind, 1968b). It would,

however, be reasonable to assume that at dilute concentrations, a delay in settling could be a result of the time required to dissipate residual fluid motion resulting from filling the column or mixing to assure uniform solids distribution. Although distinct aggregates may not exist in the presence of the residual fluid motion, as the motion dissipates it would be expected that particle aggregation would be nearly instantaneous since the rate of aggregation is proportional to the square of the number of primary particles, as given by theoretical flocculation kinetics (Weber, 1972).

Intermediate suspensions At intermediate concentrations, a flocculent suspension can possess a degree of structural integrity and a variety of phenomena result. The initial period of acceleration of the interface illustrated in Figure 2 is the result of the formation of fluid paths of low resistance, i.e., channelling, to accommodate the fluid displaced from the underlying suspension as the solids accumulate in the bottom of the container. Channel formation is a rate process and a time dependent induction period exists (Scott, 1968c; Harris et al., 1975). The role of channel formation in batch thickening has been examined in detail by Dell and Kaynar (1968) and the contribution of channels to the overall permeability of a suspension has been used as a basis for the mathematical description of settling velocity versus concentration data (Michaels and Bolger, 1962; Scott, 1968c).

The maximum rates of interface subsidence following an induction period are generally taken as the settling velocities of interest and it is often unclear whether or not the various authors consider such

velocities as representative of true hindered settling or of intermediate concentration behavior. Unlike true hindered settling, the maximum velocity of an intermediate suspension is dependent upon a number of experimental test variables that result in the formation of structural networks of particles within the suspension.

The maximum settling velocity of an intermediate suspension decreases with decreasing initial suspension height--possibly as a result of support of the suspension interface transmitted from the bottom of the test column through the underlying suspension (Dick and Ewing, 1967; Gaudin et al., 1959; Michaels and Bolger, 1962). Since the initial height of a suspension will govern the time available for channels to develop, the rate process nature of channel formation could be a contributing factor of the effect of initial suspension height when small heights or long induction periods are involved.

Low energy stirring disrupts the channel formation process and prevents their formation or limits the extent to which they can form. The induction period of interface acceleration can be reduced or completely eliminated by stirring and the maximum settling velocities can be significantly lower than when channelling occurs (Dick and Ewing, 1967; Javarheri and Dick, 1969; Vesilind, 1979).

It is interesting to note that, though channelling is generally considered to occur in continuous-flow thickeners, the evidence in the literature is unsound. Coe and Clevenger (1917), Fitch (1962, 1975b), and many others apparently assumed that channelling would exist in continuous-flow thickeners because of its observed presence during batch

thickening. Chandler (1983) inferred the existence of channelling in a deep, continuous-flow thickener because of an "abnormally high" scatter of suspended solids versus depth data and because the estimated permeabilities (based on continuous-flow thickener measurements) of an apparently flocculated suspension were orders of magnitude greater than the permeabilities estimated from a filtration test of the same, but unflocculated suspension. Such a comparison would indicate the effect of the flocculant rather than the existence of channelling in the continuous thickener. Turner and Glaser (1976) cited the accumulation of water on the underside of an observation wedge in a continuous-flow thickener as evidence of channelling. The accumulation of water was more likely the result of compression and a batch-thickening type of situation in the segment of the thickener that did not receive additional solids from above.

Evidence counter to the assumed existence of channelling in a continuous-flow thickener could be inferred from the work of Scott (1968b). He found that stirring during a batch test significantly reduced the interface settling velocities at higher concentrations, which would be consistent with the effect of stirring on the channel formation process, and the resulting solids flux values were much closer to the actual fluxes occurring in a pilot-scale thickener.

Relatively small increases in suspension permeability have been considered to be channelling (Kos, 1977a,b) and as such, micro-channelling may occur in continuous-flow thickeners but the macro-channelling referred to by many appears to be unlikely in continuous-

flow thickening.

Concentrated suspensions A decreasing rate of interface subsidence over the full duration of a batch settling test is characteristic of concentrated suspensions in a compression mode of settling. At these concentrations, interparticle contacts extend throughout the settling column and the suspension exhibits compressive and shear strengths.

The batch thickening of solids in compression has been modeled using a variety of approaches. Roberts (1949) considered the interface subsidence to be a process of primary consolidation in which the rate of subsidence is proportional to the difference between the amount of fluid present at any time and the equilibrium fluid content of the fully compacted solids. This approach assumes that the resistance to settling is a function only of the permeability of the solid matrix.

Chakravarti and Dell (1970), Dell and Sinha (1966), Scott (1968c), and Shirato et al. (1970) conducted extensive investigations on the behavior of compression settling. The results revealed that the settling rate of solids undergoing compression is a function of both the permeability and the compressive stress existing in the sediment. As a result, the settling behavior, as well as the final concentration, is influenced by the height of the sediment. Test column diameter would also be expected to influence the observed interface subsidence rate due to the support offered to the subsiding suspension by the shear stress acting at the container wall.

Low intensity stirring can alter the behavior of a suspension in

compression as a result of disruption of the structural integrity of the sediment. Higher underflow concentrations have been achieved in continuous thickeners utilizing a raking mechanism (Comings et al., 1954).

Initial settling velocity

Because of the variety of phenomena, such as compression and channel formation, which influence the batch settling characteristics of a flocculent suspension, the measured settling velocities may not be a unique function of concentration. In conducting batch settling tests to obtain data for the design of a continuous-flow thickener, settling velocities as a function only of concentration are needed and recommendations of minimum column height and diameter, and gentle stirring have been made in order to obtain those unique velocities. For dilute flocculent suspensions which undergo true hindered settling, an interface forms immediately after the dissipation of residual fluid motion and settles at an initial velocity which persists over a substantial settling depth. For dilute suspensions, therefore, there is little doubt as to the settling velocity which is characteristic of a given concentration of suspension.

For intermediate and concentrated suspensions, however, an infinite number of velocities can exist for a given concentration because of the possible dimensions of the test column and the characteristics of low intensity stirring, when used, and because of the segment of the settling curve which is chosen as characteristic. For example, Michaels and Bolger (1962) considered the maximum velocity that occurred during a

test as the velocity of interest. Vesilind (1968b), in describing a typical settling test, considered the constant rate of fall following an induction period as the characteristic velocity.

A possible characteristic velocity that has up to now eluded the attention of researchers could be called the initial settling velocity. This would correspond to the rate of interface subsidence prior to the onset of the channel formation process in unstirred, intermediate suspensions, but following the dissipation of residual fluid motion and particle aggregation.

To illustrate the effect of initial suspension height on the maximum settling velocity of an intermediate suspension, Michaels and Bolger (1962) presented four interface height versus time plots. The maximum settling velocities increased with depth, but the initial rates of interface subsidence, though significantly lower than the maximum rates, were nearly equal, with but one exception, and no initial suspension height effects were apparent.

Data presented by Gaudin et al. (1959) also indicate the possible existence of a characteristic initial settling velocity which is independent of column depth.

Scott (1968c) compared the batch interface subsidence curves obtained with and without stirring. The unstirred test resulted in an obvious induction period followed by a constant rate of subsidence. The stirred test did not have an induction period and the constant settling velocity that resulted closely approximated the initial settling velocity of the unstirred test.

The interface subsidence for concentrated suspensions is characterized by a continually decreasing rate of subsidence. Fitch (1979) and Kos (1980) presented discussions that considered the possibility of concentrated suspensions possessing maximum permeabilities that are a function of concentration only. These maximum permeabilities would be evident as characteristic settling velocities, however, only if initial suspension heights are large enough such that compressive resistance to subsidence was nonexistent. Upflow experiments that would duplicate those conditions have been proposed as a method of investigating the characteristic maximum permeabilities.

Shirato et al. (1970) presented interface subsidence curves for different depths of a concentrated suspension. They noted that the initial rates of interface subsidence were, in fact, equal although the subsidence rates at later times were depth dependent. This observation was classified as an impossible occurrence for concentrated suspensions by Fitch (1979) due to the compressive forces that must be present in concentrated suspensions. However, pressure measurements made by Shirato et al. (1970) revealed that, initially, no measurable compressive forces were present.

The hydrodynamic conditions present during the first few minutes of batch settling, regardless of the concentration range, may be a distinct function of concentration and may, therefore, be of importance to gravity thickening.

Settling velocity-concentration relationships

This author is not aware of any theoretical or semi-theoretical settling velocity-concentration relationships that are applicable to a wide range of flocculent suspension concentrations. This, however, would be expected as a result of the distinct differences in settling behavior that occur for dilute, intermediate, and concentrated flocculent suspensions. Settling velocity relationships of a semi-theoretical nature have been developed for, or applied to, specific concentration ranges. Additionally, two empirical velocity-concentration relationships have been frequently applied to the settling of activated sludge.

Flocculent hindered settling Up to some limiting concentration, flocculent suspensions undergo hindered settling as a collection of aggregates or flocs. Michaels and Bolger (1962) demonstrated that a velocity-voidage correlation developed for hindered settling of spherical particles could be used to model the velocity versus concentration relationship up to a concentration at which it was presumed that the aggregates were numerous enough for contact and structural integrity to occur. The velocity-voidage correlation was that of Richardson and Zaki (1954) and a modified form was used that related the velocity versus concentration data to the aggregate properties of size and density.

For sedimentation in creeping flow for which the intercept velocity is equal to an isolated particle's terminal settling velocity (neglecting the effect of column diameter), the correlation of

Richardson and Zaki, Equation (5), becomes:

$$v/v_o = \epsilon^{4.65} \quad (14)$$

Michaels and Bolger (1962) observed that the settling units of a flocculated kaolinite suspension were individual aggregates and the effective porosity of the suspension would therefore be the interaggregate porosity and not the overall suspension porosity. They expressed Equation (14) as:

$$v = v_o (1 - \phi_a)^{4.65} \quad (15)$$

where ϕ_a = aggregate volume concentration. Noting that $\phi_a = K\phi_s$, where K = volume of aggregate per volume of solids and ϕ_s = solid volume concentration, Equation (15) was rearranged to give:

$$v^{1/4.65} = v_o^{1/4.65} - v_o^{1/4.65} K \phi_s \quad (16)$$

which is a linear equation of $v^{1/4.65}$ versus concentration, ϕ_s , with intercept of $v_o^{1/4.65}$ and slope of $v_o^{1/4.65} K$. For the flocculated kaolinite systems examined, the interface velocity versus solid volume concentration data were indeed linear up to solid volume concentrations ranging from 0.005 to 0.1.

The significance of Equation (16) is that the hindered settling velocities of flocculated suspensions can be correlated with the suspension concentration rather than the interaggregate porosity as would be required if other available hindered settling velocity relationships were used. The mass concentration can also be used in Equation (16) by assigning the dimensions of volume of aggregate per

mass of solid to the variable K.

There are several instances in the literature for which the Richardson and Zaki correlation has not been correctly applied to flocculent hindered-settling systems which resulted in conclusions that questioned the validity of the correlation.

Davies et al. (1976), Dollimore et al. (1972), and Lawler et al. (1983) attempted to correlate settling velocity data according to Equation (4) by plotting $\log V$ versus $\log \epsilon$. In all instances, the overall suspension porosities were apparently used and not the interaggregate porosity which is the effective porosity for flocculent hindered settling. Correlating the flocculent hindered-settling velocity with the interaggregate porosity as given by Equation (4) would be valid. And, hindered settling correlations based on velocity as a function of porosity developed by others would also be expected to be in agreement with experimental data if interaggregate porosity were used. However, for flocculent suspensions, the interaggregate porosity as a function of concentration is, in itself, an unknown and therefore correlations expressible only in terms of effective porosity are of little practical significance to flocculent hindered settling.

For the hindered settling of uniform spheres, Steinour (1944a) assumed a model similar to a porous medium in which the size and shape of the flow paths were a function of the porosity. His result was

$$V = V_o \frac{\epsilon^3}{1-\epsilon} f(\theta) \quad (17)$$

where the function $f(\theta)$ was defined as a porosity dependent shape factor for the flow paths within the porous bed. This correlation was found to be valid for angular particles when a correction term was subtracted from the porosity (Steinour, 1944b). The correction term was believed to represent an amount of immobile liquid that was associated with each particle. Subsequent work (Steinour, 1944b,c) revealed that the hindered settling of flocculent suspensions could be similarly correlated with concentration when the correction term was used.

Empirical correlations

Two empirical velocity-concentration relationships have been widely used to model the settling behavior of flocculent suspensions. They are

$$V = \alpha C^{\beta} \quad (18)$$

and

$$V = V_0 \exp(\gamma C) \quad (19)$$

where α , β , and γ are constants. Their usefulness lies in the fact that settling velocity versus concentration relationships of these two forms allow for analytical solutions to thickener design and operation based on solids flux theory (Baskin and Suidan, 1985; Dick and Young, 1972).

The literature is neutral as to a preference for either Equation (18) or (19). The choice depends upon the degree to which the model fits the experimental data. It appears, though, that Equation (19) may be more appropriate in the vicinity of the concentration at which the maximum gravity flux occurs, whereas Equation (18) provides a better fit at higher concentrations, as evidenced by the data presented by Baskin

and Suidan (1985).

Particle Aggregation in Thickening

The formation of aggregates or flocs of primary particles plays a fundamental role in determining the settling behavior of flocculent suspensions. For dilute suspensions in which hindered settling occurs, the settling units are aggregates and the hindered settling velocity is a function of the size, shape, density, and volume concentration of the aggregates. The effect of changes of the flocculent nature of a suspension on the observed settling behavior is, therefore, a result of changes in the aggregate properties. The observed behaviors of intermediate and concentrated suspensions have been conceptually modeled by assuming that compression and splitting of the aggregates occur.

Aggregate properties from settling velocity data

Michaels and Bolger (1962) extended the utility of Equation (16) to the estimation of the size and density of the individual aggregates present during flocculent hindered settling by expressing V_o by Stoke's Law for the terminal settling velocity of a spherical aggregate in creeping flow:

$$V_o = \frac{g(\rho_a - \rho_l)d_a^2}{18\mu} \quad (20)$$

where ρ_a = aggregate density and d_a = aggregate diameter. The intercept and slope of Equation (16) were then solved for K. Noting that K is a function of the primary particle and aggregate densities, the aggregate

diameter and density were then estimated.

The estimated aggregate properties were in qualitative agreement with their expectations for the particle associations that were predicted as a function of pH and electrolyte concentration of the aqueous kaolinite systems that were investigated. Conditions favoring edge-to-face platelet associations produced larger aggregates of lower density than for conditions favoring face-to-face platelet associations.

Michaels and Bolger did not attempt to verify the estimated aggregate properties rigorously, presumably due to the obvious difficulty of measuring moving objects with the aid of magnification. They did note, however, that the estimated diameters were within the range of observed diameters. The validity of the Michaels and Bolger procedure has, however, been generally accepted, as indicated by the frequency with which it has been applied to the settling of flocculent suspensions and used for characterization of the aggregates formed during hindered settling (Bodman et al., 1972; Javaheri and Dick, 1969; Khatib and Howell, 1979; Scott, 1968a,b,c, 1979; Shin and Dick, 1980; Shirato et al., 1970).

Fouda and Capes (1979) applied the correlation of Richardson and Zaki to the hindered settling of flocculent suspensions for the case of Reynolds numbers greater than 0.2. The general correlation:

$$V = V_o (1 - K\phi_s)^n \quad (21)$$

was used where V_o and n were known functions of the Reynolds number.

Published polynomial relations for the terminal settling velocity as a

function of Reynolds number, and the expressions originally presented for n (Equations (8) and (9)), excluding the effect of column diameter, were used. The determination of V_o , K , and n for a given set of data required a trial and error procedure. Upon reanalysis of the data presented by Michaels and Bolger (1962), one case for which creeping flow ($Re < 0.2$) did not occur was found. For that suspension the Reynolds number of an isolated particle was 0.25 and the terminal settling velocity as calculated assuming $Re < 0.2$ was about 9% greater than calculated with the trial and error procedure. The aggregate diameter and density estimates were similarly greater. The two methods generally agreed for the other suspensions for which $Re < 0.2$, but the estimates deviated as Re approached 0.2.

Matsumoto et al. (1980) investigated the hindered settling of an activated sludge flocculated with a cationic polyelectrolyte and applied the correlation of Richardson and Zaki. The particle Reynolds numbers were in the range of 2 to 30 and n , as given by Equation (10), was used (again neglecting the effect of column diameter). The solution of Equation (21) required a trial and error procedure that relied on measurements of the terminal settling velocities of isolated aggregates as a function of diameter.

The aggregate diameter estimates obtained from the solution of Equation (21) for the velocity-concentration data at several dosages of polyelectrolyte were compared with measured aggregate diameter distributions. The measured median aggregate diameters were 2 to 5 times larger than the corresponding estimates, but the significance of

this disagreement is difficult to evaluate based on the information that was presented. They did note, however, that internal flow within a permeable settling body would result in a higher settling rate than for an impermeable body. Intraggregate flow during hindered settling could, therefore, have resulted in the estimated diameters being lower than the measured values, but this possibility was not put forth by the writers. Intraaggregate flow was, however, cited as being responsible for a less than expected increase in the settling velocity of the activated sludge upon the addition of the polyelectrolyte.

Effects of flocculent nature and pretreatment mixing

The effects of varying conditions of flocculent nature on the batch settling behavior of a variety of suspensions have been reported in the literature and many of the investigators interpreted the results using "estimated" aggregate sizes and densities. In the majority of the investigations, however, more than one of the variables of flocculent nature were changed simultaneously. The works of Michaels and Bolger (1962) and Khatib and Howell (1979) using kaolinite were complicated by changes in the nature of the clay platelet associations with changing pH and electrolyte conditions. Dollimore et al. (1972) reported on the effect of different types of organic flocculants, as did Pearse and Barnett (1980). Bodman et al. (1972) presented limited data on the effects of pH, salt concentration, and organic flocculant dosage on the batch settling behavior and aggregate characteristics of a titanium dioxide suspension in addition to the effects of the dissolved alumina content on the behavior of an alum mud.

Sadowski et al. (1978) conducted a systematic investigation on the effect of pH, and, therefore, surface potential of ground quartz suspensions of three sizes. Aggregate sizes were estimated using a velocity-concentration relationship-based method that had been demonstrated by Dollimore and co-workers (Dollimore et al., 1972; 1973). The method involved correlating the velocity concentration data by:

$$\log v = mw + \log a \quad (22)$$

where m and a are constants and w is the weight percent concentration. The intercept value a is set equal to the unhindered velocity of an isolated aggregate and Equation (20) is then used to estimate the aggregate diameter---apparently assuming an aggregate density equal to that of the primary particles. This procedure suffers from the serious flaws of the over estimation of unhindered settling velocity and the use of the primary particle density in calculating the aggregated diameter.

Though Sadowski et al. (1978) apparently presented sufficient data for reanalysis and estimation of aggregate characteristics based on Equations (16) and (20), the reanalysis has not been done at this time. The effect of pH on settling velocity was as would be expected, the maximum velocity at a given concentration occurred at the pH corresponding to a surface potential of zero.

Matsumoto et al. (1980) estimated the size and density of activated sludge aggregates flocculated with a cationic polyelectrolyte. They concluded that the settling velocities that increased with increasing flocculant dosage were primarily the result of increased aggregate

diameters rather than aggregate densities. At sufficiently high flocculant dosages, suspension restablization and a decrease in settling velocity occurred. It should be noted that the dosages of flocculant (mass per unit suspension volume) were held constant and therefore the ratio of flocculant per unit of activated sludge solids was not constant for a given set of velocity-concentration data.

The effects of pretreatment mixing on aggregate size and density have not been detailed in the literature. Effects of pretreatment mixing have been reported only as preliminary results that were of concern with respect to the experimental procedure and reproducibility of results. Michaels and Bolger (1962) reported that high intensity mixing resulted in higher settling velocities than were observed for gently mixed suspensions. Their data did indicate a significant concentration of solids in the supernatant of the intensely mixed suspension. Because their comparison of velocities was based on initial suspension concentration, their conclusion regarding an increase in velocity with pretreatment mixing intensity could have been unfounded. It is interesting to note, however, that the effect of mixing was reversible in that a series of tests of varying pretreatment mixing intensity conducted using the same suspension resulted in settling velocities that were a function only of the most recent mixing conditions.

Bodman et al. (1972) found that mixing intensity had no effect on the settling velocities of titanium dioxide suspensions which were flocculated by surface potential control using pH adjustment only. The

mixing conditions were the same as those compared by Michaels and Bolger (1962). The results of Bodman et al. would indicate that the aggregate characteristics of the settling titanium dioxide suspensions were independent of prior mixing.

Pearse (1980) reported an increase in the settling rate of a polymer-flocculated kaolinite suspension corresponding to a decrease in duration of gentle mixing following flocculant addition. The effect of pretreatment mixing conditions on the settling velocity, and presumably the aggregate characteristics, of a polymer flocculated suspension could be the result of effects of mixing on the distribution and arrangement of the polymer molecules on the particles.

Aggregate variations during thickening

The thickening behaviors of intermediate and concentrated suspensions have been explained by conceptual models involving the compression and/or splitting of the aggregates that form during flocculent hindered settling.

Michaels and Bolger (1962) considered two levels of aggregation in an aqueous kaolinite system. The primary flow units of flocculent hindered settling were assumed to be aggregates of smaller floccules of primary particles. Flocculent hindered settling was characterized by constant aggregate characteristics with varying interaggregate porosity up to some limiting concentration. For suspensions of intermediate concentrations, the aggregate size and density were assumed to remain unchanged and the decrease in maximum settling velocity with increasing concentration was believed to be the result of an increase in

interaggregate attachments in addition to a decrease in interaggregate porosity. The behavior of concentrated suspensions was felt to be the result of aggregate compression and the release of intraaggregate water, and the ultimate settled density was assumed to represent the close packing of spherical floccules to an interfloccule porosity of 0.62.

Scott (1968a,b, 1970) explained the continuous-flow thickening behavior of flocculent suspensions in terms of aggregate deformation and compression. He presented solids flux data on a dimensionless basis in which the solids concentration was expressed in terms of aggregate volume concentration, ϕ_a , (volume of aggregates per unit suspension volume) using the ratio of aggregate volume to solids volume as determined for the dilute concentration range of flocculent hindered settling. In intermediate suspensions of ϕ_a greater than 0.3 to 0.5, deformation, but not compression, of aggregates was believed to occur. The behavior of concentrated suspensions of ϕ_a greater than 0.92 to 1.1 was attributed to the collapse and compression of the deformed aggregates.

The conceptual model of Harris et al. (1975), that was restated by Akers (1980) and Somasundaran (1981), for the batch thickening of intermediate and concentrated suspensions was also based on the deformation of aggregates to achieve a more dense packing arrangement.

It is interesting to note that the above conceptual models are based on an implicit assumption that only one size and density of aggregate is possible for any given suspension and that for concentrations greater than the flocculent hindered settling range, the characteristic aggregate retains its individuality although its size,

shape, and density can change. If these conceptual models were based only on continuous-flow thickening data or the data derived from a single batch settling test in which the initial conditions were flocculent hindered settling, then the assumption of maintenance of individual aggregate identity may have been valid. However, much of the work was conducted using a series of individual settling tests over a wide range of concentrations--a range of settling conditions for which it would be difficult to imagine that only one size of aggregate would be possible.

Figure 3 illustrates typical settling velocity versus suspension concentration data plotted according to Equation (16). The linear portion of the plot represents the flocculent, hindered settling of aggregates whose size and density can be estimated from the slope and intercept. Javaheri and Dick (1969) proposed the application of Equation (16) to higher suspension concentrations for which $v^{1/4.65}$ versus C was nonlinear. From the slope and intercept of a tangent to the velocity-concentration curve, the aggregate size and density at some higher concentration, C_1 , could be estimated. A necessary assumption, however, would be that the settling velocity is a function of concentration only.

Strong objections to this application of the Richardson and Zaki correlation as modified by Michaels and Bolger were expressed by Fitch (1975b, 1979). In his 1975 paper, Fitch objected to the validity of Javaheri's and Dick's tangent construction procedure on theoretical grounds, but he cited experimental evidence only as proof. It is

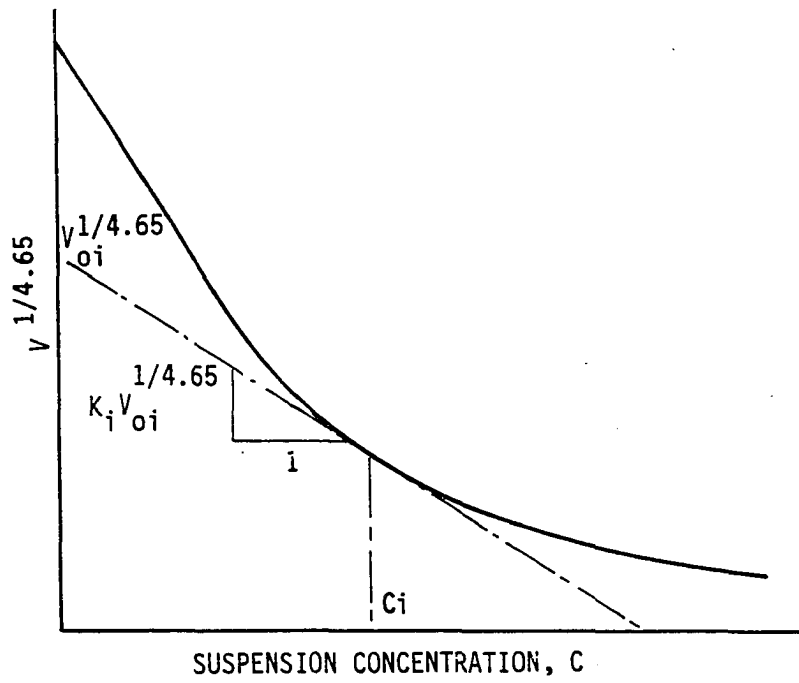


Figure 3. Typical interface settling velocity data, plotted according to Equation (16), illustrating the tangent construction procedure for aggregate property estimation

apparent to this author, however, that the experimental evidences cited by Fitch were simply examples of conditions for which the settling velocities were not a unique function of concentration. Therefore, the citations were merely examples of conditions for which the necessary assumption of velocity dependence was not valid and, thus, they did not represent a failure of the concept.

In his 1979 paper, Fitch attempted to refute the tangent construction procedure based on theoretical grounds. He concurred that changes in aggregate diameter and density with concentration would result in nonlinear $V^{1/4.65}$ versus C behavior due to changes in the intercept and slope of Equation (16). He went on to state that the slope at any point would, therefore, not measure the effect of concentration alone based on a total derivative of the change in $V^{1/4.65}$ with respect to C that he presented which included terms for the change in $V_o^{1/4.65}$ and K with respect to C . However, the purpose of the tangent construction procedure is not to measure the effect of C alone, but to estimate the aggregate diameter and density that are the result of constraints which are placed on the system of aggregates by a concentration dependent mechanism. Indeed, the effect of C alone on hindered settling of flocculent suspensions for which aggregate diameter and density are constant has already been established. Fitch, therefore, provided additional support for interpreting curvilinear $V^{1/4.65}$ versus C behavior as the result of some effect of concentration on the properties of the aggregates of a flocculent suspension.

Javaheri and Dick (1969) used their tangent construction method to

estimate the aggregate properties of three activated sludges as a function of concentration. The results were admittedly of a qualitative nature only because of the size of the test columns that were used. Individual settling tests at each concentration were conducted in both stirred and quiescent columns. The velocity of interest was that of the extended constant rate period following an initial, short period of induction.

For these sludges, stirring increased the rate of interface subsidence above a certain concentration which would indicate that the unstirred velocities were artificially low due to the relatively shallow depth of the columns and that, if channelling occurred, it was not totally eliminated by stirring.

The apparent trends in the aggregate property changes, which were the same for the three biological sludges, were as follows:

1. an increase in aggregate density with increasing concentration,
2. a decrease in aggregate diameter with increasing concentration,
- and
3. a decrease in interaggregate porosity with increasing concentration.

A conceptual model that included aggregate compression and splitting was used to interpret the results. Again, as with the conceptual models of others that were discussed previously, an implicit assumption was that only one size and density of aggregate was possible in the absence of compressive and shear forces.

Shin and Dick (1980) applied this tangent construction method to

the settling of a calcium carbonate suspension as part of an investigation in which the applicability of the ideal thickening theory of Kynch (1952) to the analysis of flocculent suspension behavior was examined. The general variations in aggregate properties with concentration were again the same as had been determined by Javaheri and Dick (1969) for activated sludge. It is significant to note that, although the observed changes in aggregate properties with concentration were believed to be responsible for some of the discrepancies between the flux curve obtained by a series of tests over a range of concentrations and the flux curve based on the application of Kynch's theory to a single settling test, the authors felt that similar changes in aggregate properties occurred during the declining rate portion of a single batch settling test because of the overall agreement obtained between the two methods of flux curve generation.

In their study of activated sludges, Javaheri and Dick (1969) also applied the Carman-Kozeny velocity-voidage relationship in a similar fashion and obtained aggregate property results that were in agreement with the results of the tangent construction method based on Equation (16). The use of the Carman-Kozeny equation was, however, subject to two disadvantages--an inability to calculate the aggregate diameter because of an unknown constant and unrealistic behavior of the velocity-voidage correlation at low concentrations.

Shin and Dick (1975) applied the Carman-Kozeny based method of aggregate property estimation to the batch thickening of a lime-softening sludge at concentrations for which solids pressures existed

within the settling sludge. Aggregate diameters and densities were estimated as a function of concentration by expressing the Carman-Kozeny relationship in terms of the experimentally-measured permeability of the thickening sludge as a function of concentration.

In summary, then, above a certain minimum concentration which marks a departure from flocculent hindered settling, the diameters and densities of the aggregates formed during settling or thickening will decrease and increase, respectively. It would be expected, then, that as the concentration of a suspension is increased, the aggregate's size would decrease to some limiting value--the size of the primary particles. Any further change in suspension permeability would be the result of a decrease in interparticle porosity. This apparently occurs, as evidenced by Scott (1968c) who found that at high concentrations, well beyond the range of flocculent hindered settling, the velocity-concentration data were fit equally well by both Equation (16) and the Carman-Kozeny correlation. Particle diameter estimates ranging from $4.9\text{ }\mu\text{m}$ to $8.1\text{ }\mu\text{m}$ were obtained which were in close agreement with a measured particle diameter of $4.2\text{ }\mu\text{m}$.

Aggregate size and density

The relationship between the size and density of an aggregate, or floc, formed during the coagulation and flocculation of very dilute suspensions has been the subject of a number of investigations. Several methods of aggregate property measurement have been used and a variety of suspension types and conditions of coagulation and flocculation have been examined. A common conclusion was that the bouyant density of an

aggregate is proportional to the inverse of the aggregate diameter raised to some power, as given by:

$$(\rho_a - \rho_l) \propto d_a^{-X} \quad (23)$$

where ρ_a , ρ_l , and d_a are as previously defined and $X = \text{constant}$.

Lagvankar and Gemmell (1968) investigated the formation of iron-coagulant floc in order to verify a theoretical floc formation simulation model that had been presented by another investigator. Floc diameters were microscopically measured and densities were indicated by the absence of settling when placed in solutions of different densities. Below a certain size of floc, the exponent in Equation (23) was found to be 0.7 which was in very close agreement with the theoretical value of 0.68. For larger floc, Equation (23) was still valid, but the exponent and proportionality constant differed. This was felt to be the result of a second level of aggregation in which the observed clusters were groups of smaller flocs.

Matsumoto and Mori (1975) examined the size and density of alum coagulated bentonite and activated sludge flocs. Floc diameters were determined by optical measurements and floc densities were calculated from the weight, number, and size of a collection of flocs. Again, the results were described by Equation (23), but the applicable exponents varied from 0.9 to 1.4.

Tambo and Watanabe (1979) examined a variety of types of flocs using a photographic method for diameter measurement and densities were determined from observed settling velocities. For the density

calculations they used a modified Stoke's Law that incorporated an assumed floc sphericity of 0.8. Exponents for Equation (23) ranged from 0.7 to 1.6. A theoretical floc simulation model was presented in which the floc density was related to the primary particle characteristics by:

$$(\rho_a - \rho_l) \propto (\rho_p - \rho_l) d_p^{0.9} d_a^{-0.9} \quad (24)$$

The possibility of a transition size for which floc structure varied was also discussed.

Additional evidence for the general validity of Equation (23) for relating the aggregate diameter to its bouyant density can be obtained from the work of Thomas (1963). In contrast to the dilute-system investigations cited above, Thomas investigated the settling and rheological properties of concentrated, flocculent suspensions. For several types of suspensions, the intraaggregate void ratio (ratio of the volume of immobilized fluid to the volume of solid in an aggregate), η , was correlated by:

$$\frac{d_a}{d_{app}} = (1 + \eta)^2 \quad (25)$$

where d_{app} = the apparent primary particle diameter calculated from the primary particle's size, surface area, and size distribution. By the definition of η :

$$1 + \eta = \frac{(\rho_p - \rho_l)}{(\rho_a - \rho_l)} \quad (26)$$

Equations (25) and (26) can then be combined to yield:

$$(\rho_a - \rho_l) = (\rho_p - \rho_l) d_p^{0.5} (d_a)^{-0.5} \quad (27)$$

which is of the same form as the expression, Equation (24), obtained by Tambo and Watanabe (1979).

Because of the apparent general applicability of Equation (23) in describing the relationship between aggregate buoyant density and diameter, the aggregate properties estimated from hindered settling velocities as functions of concentration would also be expected to conform to such a relationship. As illustrated by Figure 4, this is indeed the case. The data of Figure 4 were obtained from Figures 7 and 11 of Javaheri and Dick (1969), Figure 12 of Shin and Dick (1975), and Figure 4 of Shin and Dick (1980). In preparing this figure, a liquid density of 1.0 g/cm^3 was assumed and some smoothing of the original data was done. The data for the activated sludge were for the case in which slow stirring was employed during the settling tests. When fit to Equation (23), the proportionality constants for the various types of suspensions would differ significantly. The exponent, X , however, would be nearly the same, approximately 0.6, for the three suspensions.

The calcium carbonate suspension of Shin and Dick (1980) had a reported primary particle size of $5 \times 10^{-4} \text{ cm}$. By Equation (27), and using $\rho_s = 2.65$ and an exponent of 0.6, the proportionality constant $(\rho_p - \rho_l) d_p^{0.6}$ becomes 0.017 which is equal to the intercept of the plot of $\log (\rho_a - \rho_l)$ versus $\log d_a$ at $d_a = 1 \text{ cm}$.

The experimental and theoretical aggregate size-density relationships represent a situation in which the aggregate density is a

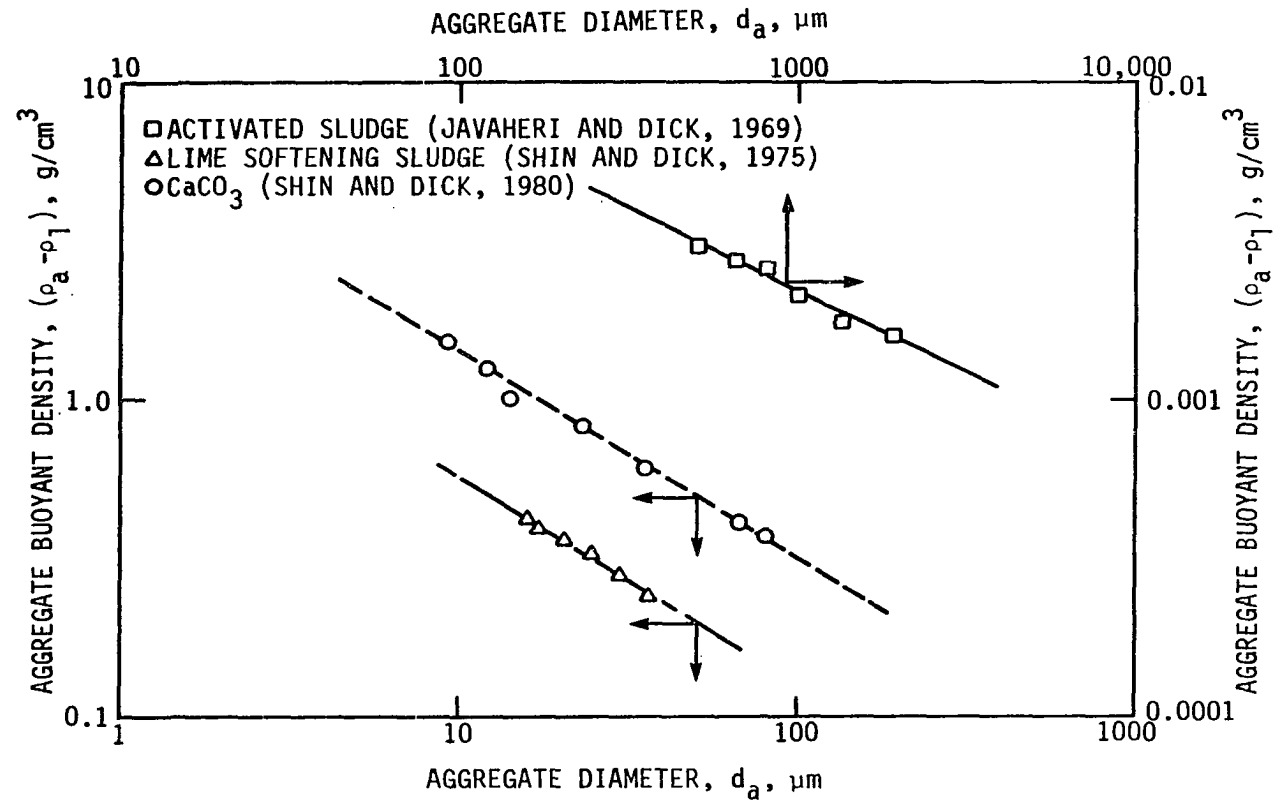


Figure 4. Aggregate buoyant density versus aggregate diameter for inorganic and biological suspensions

direct function of the diameter of the aggregate. Representations of floc structure, based on simulation models, are characterized by a dense core of closely-packed, primary particles (Lagvankar and Gemmell, 1968). As more particles accumulate, dendrite or chain-like structures form which effectively limit the penetration of primary particles into the intrafloc voids. The flocs are, therefore, not of uniform intrafloc density and the overall or average density is a function of particle diameter. It is also important to note that the conditions of fluid shear due to mixing do not alter the fundamental size-density relationship; high intensity mixing, for example, simply limits the size of the flocs or aggregates and the floc density must then necessarily increase (Lagvankar and Gemmell, 1968; Tambo and Watanabe, 1979). The aggregate diameter-density relationship as given by Equation (223) also could result in a conceptual model of aggregate variation during thickening in which compression of the aggregates need not occur to account for observed increases in density with decreasing size.

EXPERIMENTAL

Laboratory-scale, stirred, batch settling tests were conducted in order to determine the settling velocity characteristics of a flocculent suspension as a function of its degree of flocculent nature and the intensity of pretreatment mixing.

A commercially available diatomaceous earth filter aid was used as the base material of the suspension and the degree of flocculent nature of the suspension was varied by coating the base material with an organic, cationic polyelectrolyte. Initial settling velocities were measured for concentrations ranging from about 20 kg/m^3 to in excess of 200 kg/m^3 . Two intensities of pretreatment mixing and five levels of polyelectrolyte coating, representing a complete range of suspension stability, were examined.

Materials and Equipment

Suspension materials

The base material used as the primary particles in the suspension of this investigation was Celite 512, a commercially available diatomaceous earth filter aid manufactured by the Johns-Manville Corporation, Filtration and Minerals Division, Ken-Caryl Ranch, Denver, Colorado. This type of filter aid is a calcined and size classified material consisting of the intact and fragmented skeletal remains of diatoms composed primarily of silica. The particles are of angular morphology with a median particle size of $15 \mu\text{m}$ as reported by the manufacturer.

Although diatomaceous earth is, perhaps, not the most ideal base material to use in studies of thickening because of the angular nature of the particles, it was deemed appropriate for this investigation because of the quantity of material that was expected to be used. The large material requirements were the result of the use of a relatively large batch settling column, the excess suspension required per test to facilitate the chosen method of suspension preparation and handling, and a policy of nonreuse of the suspensions.

The specific gravity of Celite 512 was determined in the laboratory using standard 50 ml pycnometers with distilled water as the reference fluid. The density of a representative sample of Celite 512 averaged 2.17 g/cm^3 for four determinations.

Suspensions of Celite 512 in tap water were flocculated by the addition of Cat Floc-T, an organic, cationic polyelectrolyte with a molecular weight of 50,000 g/mole. Samples of Cat Floc-T were supplied courtesy of the Calgon Corporation of Ellwood City, Pennsylvania. Cat Floc-T was selected for this investigation because of its relatively low molecular weight which would minimize the role of bridging in aggregate formation, and because of its insensitivity to changes of pH in slightly acidic to slightly alkaline waters (Welday, 1977).

By varying the dosage of polyelectrolyte added to the suspension (expressed as grams of polymer per gram of diatomaceous earth, P/DE) it was possible to reduce the magnitude of, and reverse, the surface charge of the normally negative Celite 512 particles. The Cat Floc-T was assumed to be 100 percent active polymer by weight as received from the

manufacturer. For use in the investigation, stock solutions of 5 kg/m^3 Cat Floc-T in distilled water were prepared and a maximum shelf life of 30 days for the diluted polymer solutions was assumed.

Equipment

The batch settling tests were conducted using the stirred settling column and the necessary equipment and appurtenances for suspension preparation and transfer illustrated in Figure 5. The settling column consisted of a plexiglas tube of 4 inches (10.2 cm) I.D. and overall length of 4.4 feet (133 cm) with a bottom end plate. Sampling ports of 0.25 inch (0.64 cm) I.D. were placed at depths of 60 cm and 120 cm above the bottom of the column. The upper sampling port also served as an overflow weir which resulted in a reproducible initial suspension height of 119.7 cm. The column was equipped with a motor driven, one-rpm, four-arm stirring rake mechanism that was fabricated from 0.125-inch (0.318-cm) diameter stainless steel rods. The rods were oriented parallel with the column walls and extended from above the suspension surface to 1 inch (2.5 cm) above the bottom of the column. The rods were mounted to the central shaft using top and bottom horizontal cross-bars and the placement of the vertical rods was such that, for any two adjacent arms, there were four rods at a radial spacing of 0.438 inch (1.11 cm) center-to-center.

The suspensions were prepared and mixed in a 12 x 18 x 18 inch (width x length x depth) (30.5 x 46 x 46 cm) tank to which a 0.75 inch (1.9 cm) bulkhead fitting, for suspension withdrawal, and baffles had been added. The mixing tank baffles were 1 x 1 x 18 inch (2.5 x 2.5 x

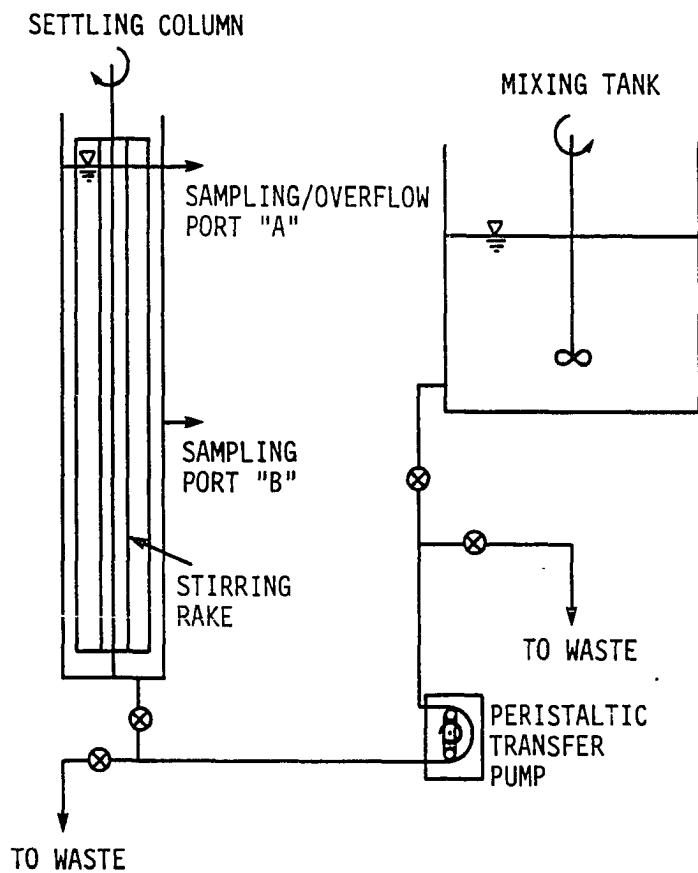


Figure 5. Schematic diagram of stirred batch settling column and necessary equipment and appurtenances

46 cm) aluminum bars placed vertically and symmetrically along the tank walls with two per side and one per end.

Suspension agitation was supplied by a Servodyne power drive system with shaft speed and torque control manufactured and assembled by Cole-Parmer Instrument Company of Chicago, Illinois. For low intensity agitation, a 4-inch (10.2-cm) diameter turbine with six 1 x 1 inch (2.5 x 2.5 cm) blades was used. For high intensity agitation, a three-bladed, 3-inch (7.6 cm) diameter propeller was employed. When used, both the turbine and propeller were placed 2 inches (5.1 cm) above the bottom and in the center of the tank.

A high-capacity, peristaltic pump (Model 3500, Sarns, Inc., Ann Arbor, Michigan) fitted with 0.75-inch (1.9 cm) I.D. tubing was used for transfer of the suspensions from the mixing tank to the settling column. All necessary tubing, valves, and connections were of a nominal 0.75 inch (1.9 cm) size.

The major piece of analytical equipment used in this investigation was a Model 102 Laser Zee Meter which had been updated to the Model 400 specifications by the manufacturer (PenKem, Inc., Bedford Hills, New York). It was used to measure the zeta potential of the suspension particles. This piece of equipment utilizes a laser for the dark-field illumination of suspended particles in a sample cell across which a voltage is applied. The electrophoretic velocity of a cloud of charged particles in the applied electric field is optically matched using a rotating prism and the resulting zeta potential is internally calculated.

Procedures

The procedures used in conducting the batch settling tests were consistent throughout the investigation with a few minor variations. The procedures involved in a typical settling test were suspension preparation, measurement of interface settling velocity, and suspension analysis for zeta potential, pH and solids concentration.

Suspension preparation

The amount of Celite 512 to be used in a suspension was weighed and dispersed in tap water by mixing at a high intensity for a minimum of thirty minutes. The tap water was first filtered through a fiber cartridge filter and the temperature was initially adjusted to about 18.5°C so that all settling tests would be conducted at $20 \pm 1^\circ\text{C}$, after a slight temperature increase, which was typical, occurred. Each settling test required about 24 liters of suspension and the Celite 512 was added to 24 liters of water from which additional polyelectrolyte for dilution water had been withdrawn. Each settling test was identified by the nominal concentration based on the mass of Celite 512 added to 24 liters of water. The final suspension volumes were somewhat greater because of the volumes of the added polyelectrolyte and Celite 512.

The required volume of stock Cat Floc-T solution, as governed by the desired P/DE ratio, was thoroughly mixed in the additional dilution water. The dosage levels used were 3.00×10^{-5} , 6.25×10^{-5} , 2.50×10^{-4} , 5.00×10^{-4} , and 1.00×10^{-3} grams of Cat Floc-T per gram of Celite 512. The final diluted volumes of the Cat Floc-T solutions ranged from 0.5 to about 4 liters. As will be discussed later, the

dilutions to 4 liters were used in an attempt to obtain a more uniform distribution of the polyelectrolyte throughout the suspension.

The polyelectrolyte solution was added to the suspension over a period of about one minute and under the pretreatment mixing conditions specified for that particular test.

Suspension pretreatment mixing

The onset of the addition of the polyelectrolyte solution marked the beginning of the pretreatment period of controlled suspension agitation. In all tests, the duration of mixing was ten minutes. At the two-minute mark, a 200 cm³ sample was collected for pH and zeta potential measurements. Prior to the end of the mixing period, the suspension temperature was measured and the mixer shaft-speed and shaft-torque, as read directly from the mixer controller, were also recorded.

The ten-minute pretreatment mixing duration was selected for two reasons. Mixing time was not a variable in this investigation though some influence of the mixing time might be expected. It was, therefore, desirable to use a relatively long period of mixing because the possible effects of changes in mixing duration on floc size and density were presumed to be small at long times as had been demonstrated for dilute system coagulation and flocculation by Camp (1968). Additionally, the author's initial intent was to measure the pH and zeta potential prior to initiating the actual settling test and this would have required a minimum of five minutes.

Two intensities of pretreatment mixing were examined. Low intensity mixing was provided by the 4-inch diameter turbine at 50 rpm.

Under these mixing conditions with 24 liters of water at 20°C, the power requirement per unit volume was 6.42 W/m^3 ($0.134 \text{ ft-lb}_f/\text{sec-ft}^3$) which would result in a root-mean-square (RMS) velocity gradient of 102 sec^{-1} . High intensity mixing was provided by the 3-inch diameter propeller at 1250 rpm. For 24 liters of water at 20°C, the power requirement was 752 W/m^3 ($15.7 \text{ ft-lb}_f/\text{sec-ft}^3$) and the resulting RMS velocity gradient was 863 sec^{-1} . Although the lower intensity of mixing would be considered to be on the high side of mixing intensities encountered in conventional flocculation processes, preliminary evaluations indicated that a further reduction in the mixing intensity would result in the formation, and subsidence, of a suspension-supernatant interface within the mixing tank at the intermediate suspension concentrations. The selected turbine speed of 50 rpm did not eliminate settling within the mixing tank, but it reduced the severity of the problem. It should be noted that achieving the transfer of a suspension of a uniform concentration to the settling column was of concern to the author which would have been questionable if significant settling were to have occurred in the mixing tank.

Batch settling tests

After ten minutes of pretreatment mixing, the polyelectrolyte coated suspension was transferred to the settling column using the peristaltic pump. The transfer rate was approximately 8-liters per minute and the filling of the column required about 1.75 minutes to complete.

The first several liters of suspension were expelled as waste in order to purge the transfer tubing of air and water. As the column was being filled, one-half liter of suspension was collected from the lower

sampling port. Pumping of the suspension was continued until the column was nearly overflowing at which time the excess suspension was allowed to pass through the upper overflow port. A second sample of suspension consisting of the first one-half liter of the excess overflow suspension was then collected. For all but the most dilute and most flocculent conditions, the column filling rate provided sufficient fluid motion to prevent the formation of an interface, and therefore settling, during the transfer process.

Observations of the position of the solids-supernatant interface position as a function of time began when the excess suspension had passed through the overflow and overflow ceased. The resulting initial suspension height was 119.7 cm but was somewhat greater for the highly concentrated suspensions that were used. During settling, the interface position as a function of time was read from a rule attached to the column wall and was recorded at intervals of time which were governed by the rate of fall of the interface. The dilute suspensions had diffuse interfaces which settled rapidly and the interface position was recorded at one-minute intervals with an estimated accuracy of, at best, plus or minus several millimeters. Although the diffuse interfaces were perhaps several centimeters in length, it was found that the level at which a particular rod of the stirring mechanism was no longer hidden by the suspension was fairly easy to document. For the slow settling suspensions of high concentration, distinct interfaces formed and their position was recorded to the nearest 0.5 mm at two minute intervals.

In most of the settling tests that were conducted, the interface

positions were recorded for only the first ten time intervals and the tests were halted shortly thereafter. The reported settling velocity in a given test was the slope of the first ten data points, as estimated by regression analysis.

Analytical determinations

For each settling test, analyses for suspension zeta potential, pH, and solids concentration were conducted.

The zeta potential of the suspension particles was measured using the Laser Zee Meter described previously. The sample of suspension that had been withdrawn from the mixing tank was allowed to settle and a very small amount of the settled suspension was then diluted with supernatant (approximately 2 to 3 drops of suspension per 30 cm³ of supernatant) and the zeta potential of the diluted particles was measured. The voltage that was applied to the cell was varied as a function of the zeta potential of the particles in order to facilitate the determination. A minimum of five separate determinations were made of the zeta potential of the sample of diluted particles and the temperature of the sample was measured for conversion of the mean observed zeta potential to the standard condition of 20°C.

The pH of the supernatant was also measured at this time using a properly standardized pH meter with a combination electrode.

It was possible to measure the zeta potential and pH of the more dilute suspensions prior to the transfer of the suspension to the settling column because of the rapid rate of settlement. For the more concentrated suspensions, an extended period of time was required before

there was a sufficient depth of supernatant for particle dilution and pH measurement.

The solids concentrations of the two samples collected from the upper and lower sampling ports during the filling of the settling column were determined gravimetrically. After vigorous and thorough mixing to resuspend the solids, 5 cm³ of sample was filtered through a dried and pre-weighed glass fiber filter of an effective pore size of 1.2 μm. The filter plus solids were then dried at 105°C and cooled in a desiccator before the final weighing.

Duplicate determinations were made on each sample and there were no apparent trends regarding any differences between the sample of a given test obtained from the upper and lower column sampling ports. The indication then, was that a uniform distribution of solids throughout the length of the settling column had been achieved. The reported solids concentration of a settling test was the average of the solids concentrations of the two samples collected for each test.

Pretreatment Mixing Power Requirements

Two intensities of pretreatment mixing were investigated. Low-intensity mixing was provided by the turbine at 50 rpm. For 24 liters of water at 20°C, the power requirement was 6.42 W/m³. As measured during the tests, the low-intensity power requirements ranged from 6.71 W/m³ to 2.81 W/m³ with a trend of decreasing power requirement with increasing nominal suspension concentration.

High-intensity pretreatment mixing was provided by the 3-inch propeller at 1250 rpm which had a power requirement of 752 W/m³ for 24

liters of water at 20°C. The high-intensity power requirements ranged from 725 W/m³ to 786 W/m³, with one exception of 942 W/m³ at the highest nominal suspension concentration used, and the power requirements increased with increasing nominal suspension concentration.

Although the effects of nominal suspension concentration on the power requirements for high- and low-intensity pretreatment mixing appear to be at odds, the effects can be explained, at least in part, by considering the variables that affect the power requirements of stirred vessels. In addition to the geometrical characteristics of the system and the type and speed of the impeller, the power required is a function of the fluid density and viscosity (McCabe and Smith, 1976). The high-intensity mixing conditions were fully turbulent and for such conditions, the power requirements are proportional to the fluid density. An increase in suspension concentration would result in an increase in fluid density and therefore an increase in power requirement would be expected and was observed.

Under the laminar or transition Reynolds number ranges, which would be characteristic of the low-intensity pretreatment mixing, the power requirement is a function of the fluid viscosity in addition to the fluid density. For an analysis to be made, the effect of suspension concentration on the ratio of density-to-viscosity would need to be determined.

It was observed, however, that at the higher suspension concentrations with low-intensity mixing, which corresponded to the lowest of the low-intensity power requirements, a supernatant-suspension

interfaced formed, and subsided, in the mixing tank. It was also observed that there appeared to be no transfer of momentum from the suspension to the overlying supernatant. The effective volume of energy dissipation was therefore less than 24 liters and the power requirement would be reduced, as was observed.

Superimposed onto the effects of suspension concentration on the fluid properties would be the increase in suspension volume with increasing nominal suspension concentration due to the volume of the Celite 512 added to a fixed volume of water. This would tend to reduce the power requirements on a per volume basis.

Because of the ranges of power requirements that occurred, the low- and high-intensity mixing will be numerically specified by the zero-solids values of 6.42 W/m^3 and 752 W/m^3 , respectively.

Suspension Characteristics

Both the pH and the zeta potential of a suspension were a function of the nominal suspension concentration. The suspension pH ranged from about 9 at the lower concentrations and decreased with increasing concentration to around 7.5 as illustrated by Figure 6. The data of Figure 6 are a partial, but typical, representation of the data collected. The nominal suspension concentration used for Figure 6 is defined as the mass of Celite 512 added to 24 liters of water and does not reflect the volume change upon the addition of the solids. The suspension pH was not affected by the polyelectrolyte dosage or the mixing intensity.

The measured zeta potentials, corrected to 20°C , as a function of

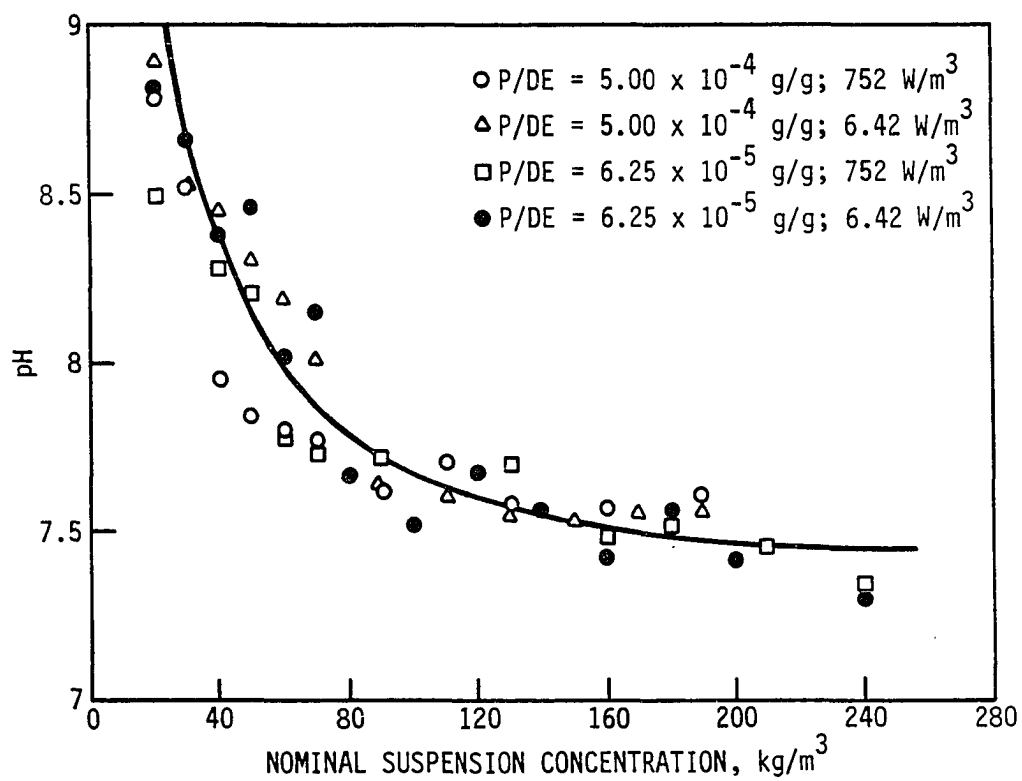


Figure 6. Supernatant pH versus nominal suspension concentration

nominal suspension concentration and polyelectrolytic dosage are presented in Figures 7 and 8. Polyelectrolyte dosage ranging from 3.00×10^{-5} g/g to 1.00×10^{-3} g/g resulted in zeta potentials which ranged from -40 mV to +25 mV. The zeta potential of uncoated Celite 512 in tap water was -58 mV at 20°C. The data of Figure 7 are for high intensity pretreatment mixing and a trend of more negative zeta potentials with increasing nominal suspension concentration is apparent.

The inability to maintain a constant zeta potential over a wide range of suspension concentrations was of concern and was pursued further as illustrated by the data of Figure 8 for polyelectrolyte dosages of 5.00×10^{-4} and 6.25×10^{-5} g/g. From the data of Figure 8, comparisons were made between the conditions of high- and low-intensity pretreatment mixing, final polymer dilutions to 1 liter and to 4 liters, and two durations of pretreatment mixing and it was concluded that:

1. at a polyelectrolytic dosage of 6.25×10^{-4} g/g, increasing the pretreatment mixing intensity from 6.42 W/m³ to 752 W/m³ had little or no effect,
2. at a polyelectrolyte dosage of 5.00×10^{-4} g/g, high intensity mixing resulted in a more positive zeta potential, and
3. neither the final polyelectrolyte dilution, nor the duration of pretreatment mixing, had an effect on the measured zeta potential.

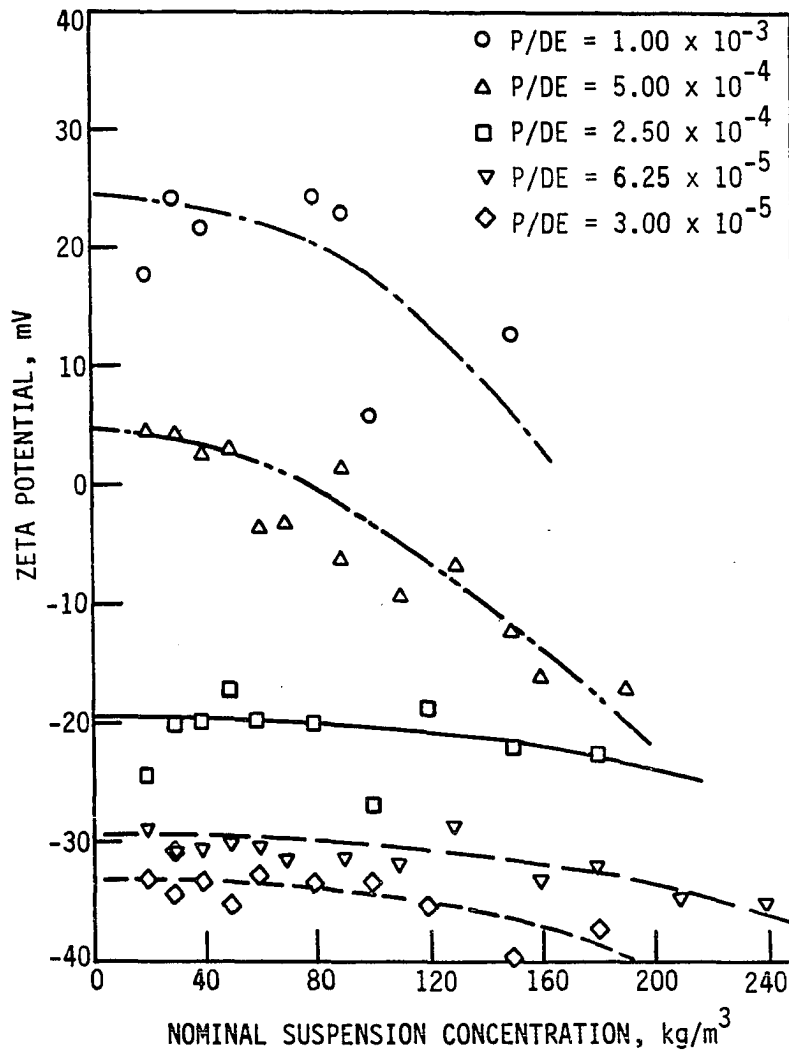


Figure 7. Suspension zeta potential versus nominal suspension concentration for various polyelectrolyte dosages and a pretreatment mixing intensity of 752 W/m^3

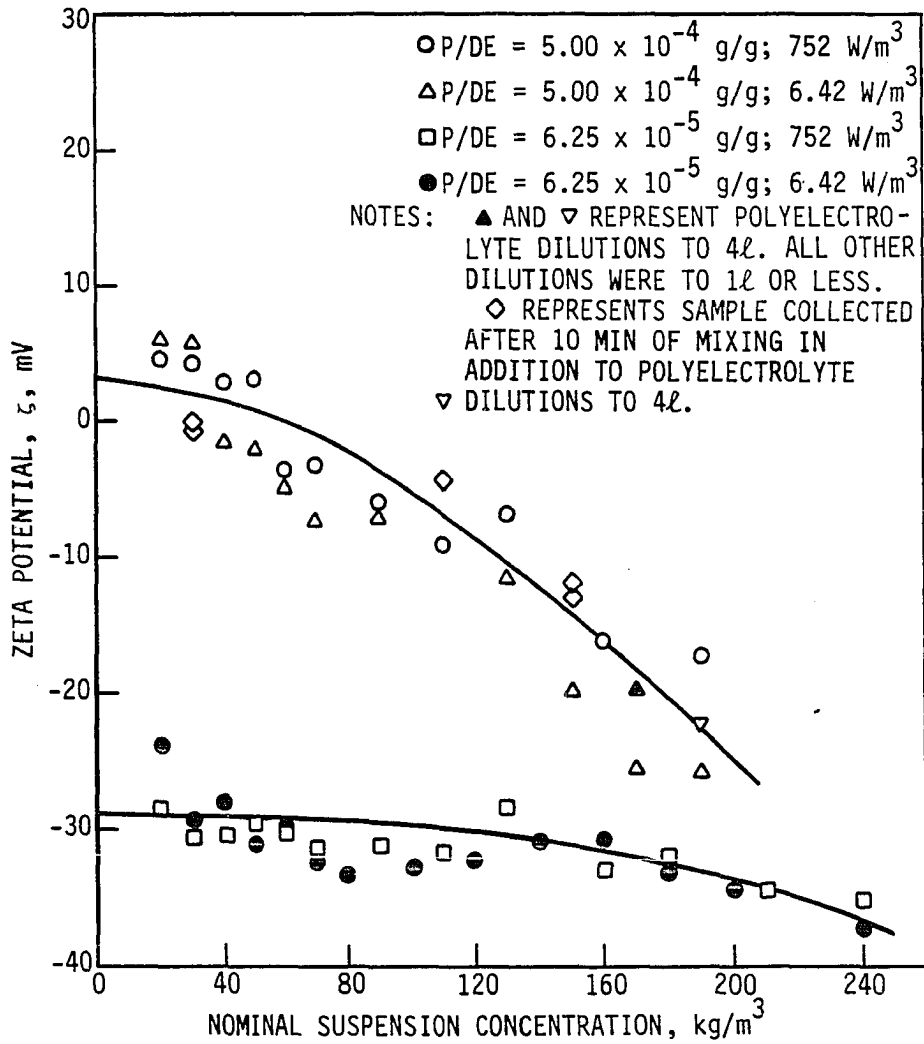


Figure 8. Suspension zeta potential versus nominal suspension concentration for polyelectrolyte dosages of 6.25×10^{-5} g/g and 5.00×10^{-4} g/g as functions of pretreatment mixing intensity, polyelectrolyte dilution, and duration of mixing

The effect of concentration on the measured zeta potential of a suspension was felt to be the result of the lack of uniformity of distribution of the polyelectrolyte molecules among the particles of the suspension. This would be supported by the second conclusion listed above. The possible effect of a decrease in suspension pH with increasing suspension concentration was assumed to be slight because of the insensitivity to pH that this particular type of polyelectrolyte exhibits at the pH values encountered in this investigation (Welday, 1977). The effect of pH on the zeta potential of uncoated particles was also assumed to be of little significance. Silica based materials generally exhibit little sensitivity to pH in slightly alkaline waters and the zero point of charge for these materials occurs under acidic conditions. A decrease in pH would, therefore, result in a more positive surface charge rather than a more negative charge as would be required to explain the observed trends of the measured zeta potential as a function of concentration on the basis of pH variations with nominal suspension concentration.

Additionally, it was noted that at the higher suspension concentrations, it was more difficult to measure the zeta potential of the particles using the Laser Zee Meter because of an apparent increase in the range of zeta potentials of the individual particles. The investigation of the effect of suspension concentration on the measured zeta potential was not pursued further, but based on the evidence of poor polyelectrolyte distribution with low-intensity mixing, it was decided that settling tests that were yet to be performed would be

conducted with a final polyelectrolyte dilution of 4 liters and high intensity mixing would be used for tests conducted at polyelectrolyte dosages other than 6.25×10^{-5} g/g and 5.00×10^{-4} g/g.

RESULTS AND ANALYSIS

More than one-hundred batch-settling tests were conducted over the course of this investigation. The primary data that were collected were the initial settling velocities of the suspensions as a function of suspension concentration from which aggregate properties were estimated. Typical results illustrating the batch settling characteristics of the suspensions will be presented followed by a presentation of the aggregate property analyses and results. The experimental and calculated data of this investigation have been included in Tables A-1 through A-8 of the Appendix.

Batch Settling Behavior

Typical batch settling characteristics of the polyelectrolyte coated Celite 512 suspensions are illustrated by Figure 9 in which interface height is plotted versus time for suspensions coated with 5.00×10^{-4} g/g of polyelectrolyte at a mixing intensity of 752 W/m^3 . Induction periods of initial interface acceleration did not occur and the transition from dilute suspension behavior, characterized by a rapid rate of interface subsidence over an extended distance, to a very low rate of interface subsidence, characteristic of concentrated suspensions, was gradual. The effect of polyelectrolyte dosage on the interface height versus time characteristics of a given concentration of suspension is illustrated in Figure 10. In comparing the interface height versus time behavior of polyelectrolyte dosages of 5.00×10^{-4} g/g and 2.50×10^{-4} g/g, a tendency to form a less dense sediment at the

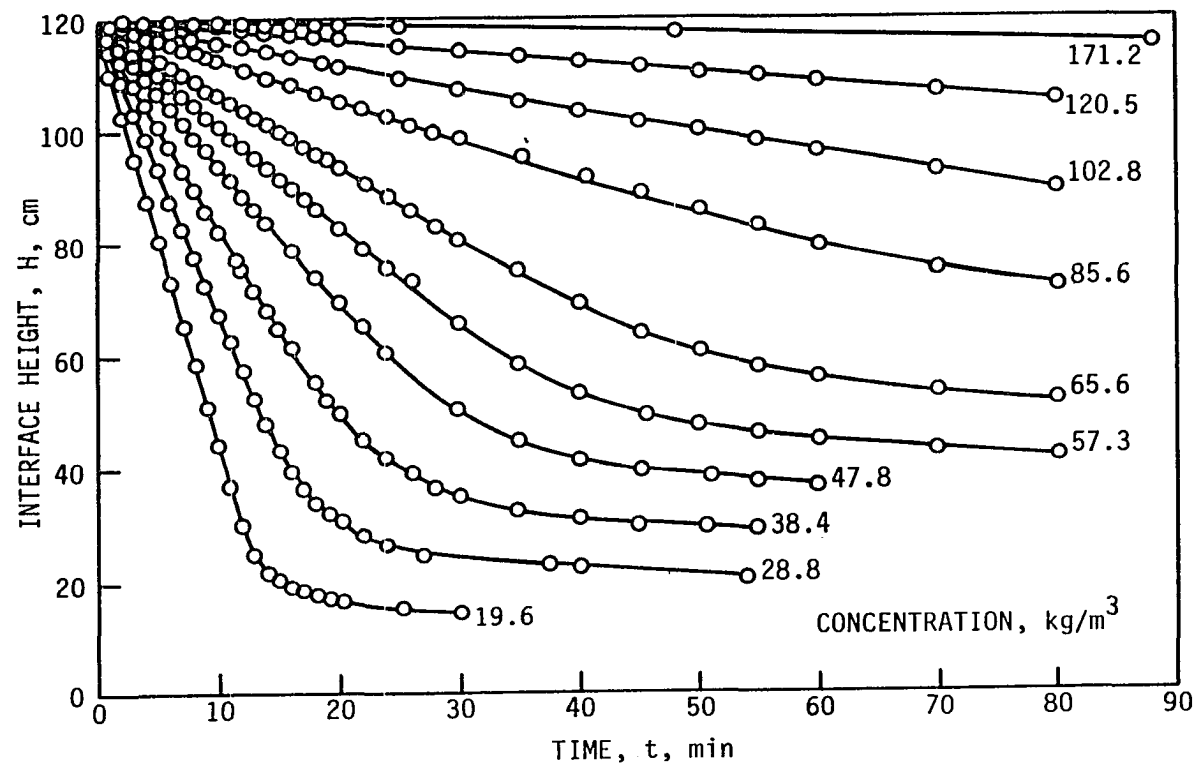


Figure 9. Interface height versus time as a function of concentration for Celite 512 coated with 5.00×10^{-4} g/g of polyelectrolyte at a mixing intensity of 752 W/m^3

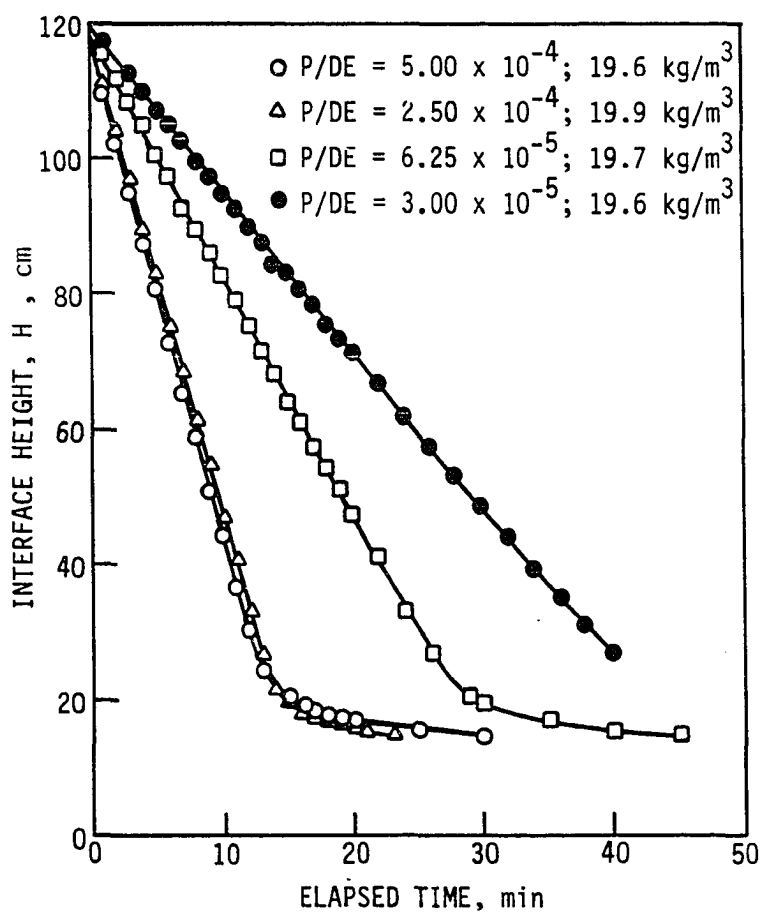


Figure 10. Interface height versus time as a function of polyelectrolyte dosage for a suspension concentration of 20 kg/m³ and high intensity pretreatment mixing

lower polyelectrolyte dosage is indicated.

The ultimate density of a sediment would be expected to vary inversely with the degree of flocculent nature of the suspension and this was verified by a set of experiments that were conducted on the effects of polyelectrolyte dosage and pretreatment mixing intensity on the ultimate, settled density of a Celite 512 suspension. The sediment density tests that were conducted were of a preliminary nature and the detailed procedures and results will not be presented. Briefly, suspensions were prepared following the usual procedures but the suspensions were allowed to settle for several days in unstirred, 4-inch (9.8 cm) diameter columns. Several initial suspension heights were used and the more flocculent suspensions resulted in a less dense sediment and the final sediment heights were independent of the pretreatment mixing intensity.

As previously noted, the settling velocity of a given suspension was estimated by regression analysis of the first ten interface height versus time data points. Typical settling velocities as a function of concentration and pretreatment mixing intensity are presented in Figure 11 for a polyelectrolyte dosage of 5.00×10^{-4} g/g. A significant decrease in settling velocity with increasing mixing intensity occurred only over the lower range of suspension concentrations that were examined and a coincidence of settling velocities occurred at higher concentrations with the exception of a small intermediate range of concentrations over which a slight "hump" in the data occurred. During the conduct of the tests, it was observed

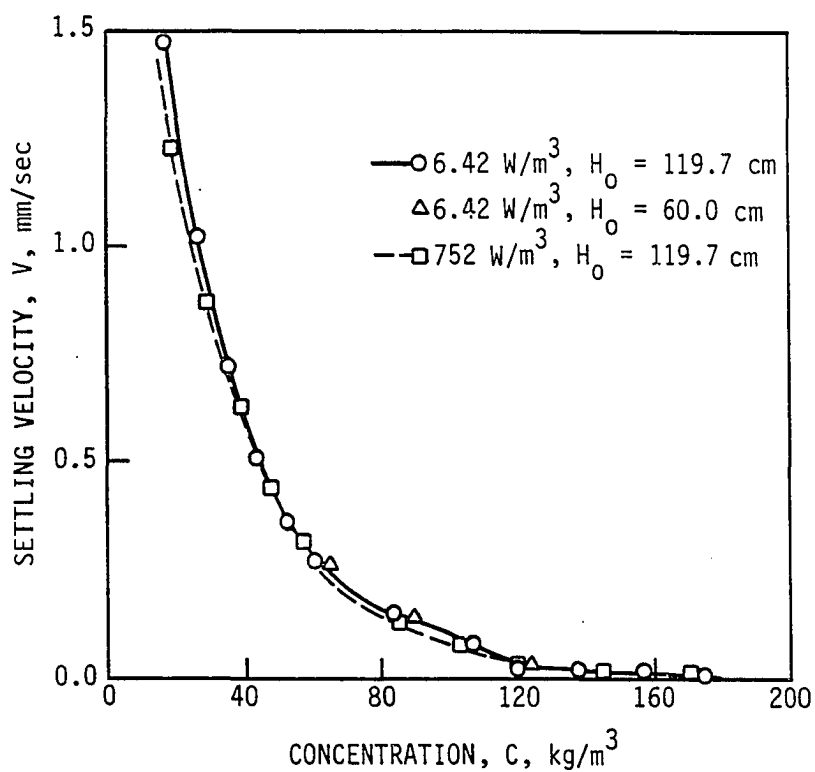


Figure 11. Initial interface settling velocity versus suspension concentration for a polyelectrolyte dosage of $5.00 \times 10^{-4} \text{ g/g}$, high and low pretreatment mixing intensities, and initial suspension heights of 119.7 cm and 60.0 cm

that the more flocculent suspensions at those intermediate concentrations (typically 60 kg/m^3 to 120 kg/m^3) possessed a secondary structure of small, discontinuous channels.

In order to establish the independence of the estimated suspension settling velocities from initial suspension height effects, additional settling tests were conducted with an initial suspension height of 60 cm. The tests were conducted for polyelectrolyte dosages of $6.25 \times 10^{-5} \text{ g/g}$ and $5.00 \times 10^{-4} \text{ g/g}$ with low intensity pretreatment mixing. The independence of settling velocity from initial suspension heights at low concentrations has been adequately established in the literature and the reduced height settling tests were therefore conducted at intermediate and higher concentrations only. The results for a polyelectrolyte dosage of $5.00 \times 10^{-4} \text{ g/g}$ are also presented in Figure 11 which show that the settling velocities were independent of initial suspension height for initial heights of 60 cm and greater. The tests conducted at the lower polyelectrolyte dosage produced the same results.

The effect of polyelectrolyte dosage on the concentration dependent settling velocity of a suspension is illustrated by Figure 12 in which settling velocities at concentrations of 20 kg/m^3 , 80 kg/m^3 , and 160 kg/m^3 are plotted versus polyelectrolyte dosage. This presentation format was chosen rather than measured zeta potential versus settling velocity because of the effect of suspension concentration on the measured zeta potential that was described previously. The data of Figure 12 are for high intensity pretreatment mixing and the data were

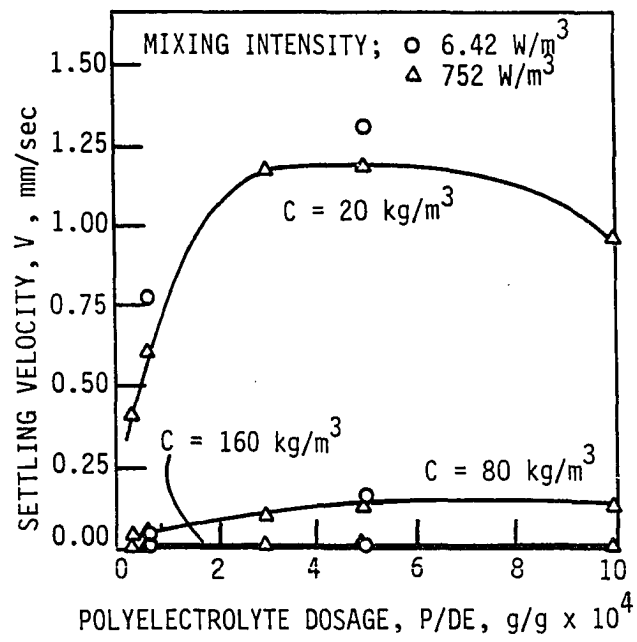


Figure 12. Initial interface settling velocity versus polyelectrolyte dosage at suspension concentration of 20 kg/m^3 , 80 kg/m^3 , and 160 kg/m^3

obtained from plots similar to Figure 10 that were drawn for each polyelectrolyte dosage. At the lower suspension concentrations, e.g., 20 kg/m^3 , the effect of polyelectrolyte dosage was as expected, the maximum settling velocity occurred at the polyelectrolyte dosage of $5.00 \times 10^{-4} \text{ g/g}$ at which the zeta potential was near zero. However, the range of polyelectrolyte dosages which resulted in a near maximum settling velocity was wide. At an intermediate concentration of 80 kg/m^3 , the magnitude in the change in settling velocity with polyelectrolyte dosage was much less than for suspension concentrations of 20 kg/m^3 , but the percentage changes in settling velocity with polyelectrolyte dosage were similar. At suspension concentrations of 160 kg/m^3 , the polyelectrolyte dosage had little or no effect.

Analysis of Settling Velocity Data

The settling velocity data for all conditions of polyelectrolyte dosage and pretreatment mixing intensity were analyzed using the modified velocity-voidage correlation of Richardson and Zaki, expressed in terms of the aggregate properties and suspension concentration as given by Equation (3). Rather than using the suspension volume concentration, Equation (3) was expressed in terms of the mass concentration C as given by:

$$v^{1/4.65} = v_o^{1/4.65} - K v_o^{1/4.65} (C) \quad (28)$$

where the variable K was redefined as

$$K = \frac{(\rho_s - \rho_l)}{\rho_s (\rho_a - \rho_l)} \quad (29)$$

Plots of $V^{1/4.65}$ versus C were constructed from which general observations were made regarding the behavior of the suspensions. Aggregate diameters and densities were then estimated for both the lower concentration ranges of flocculent hindered settling and, where appropriate, for higher concentrations using the tangent method proposed by Javaheri and Dick (1969).

Assumptions

The application of Equation (28) to the batch-settling, velocity data of a flocculent suspension requires the assumptions that:

1. the settling velocity is a function of only the suspension concentration,
2. the aggregates are of spherical and uniform size and density,
3. the Reynolds numbers of the aggregates settling at their terminal, unhindered settling velocity are less than 0.2, and
4. the ratio of aggregate diameter to column diameter is negligible.

The first assumption regarding the dependence of settling velocity on variables other than suspension concentration is related to the possible influences of batch test column height and diameter on the observed settling velocities. The occurrence of channelling within a suspension would also violate this assumption.

Slow stirring during the tests and measurement of the initial subsidence velocity occurring during the first ten to twenty minutes of a batch test were procedures that were selected in order to eliminate, or at least minimize, the effect of initial suspension height on the observed settling velocities. The selection of such procedures was consistent with the concepts and results presented in the discussion of initial settling velocities in the review of the literature. Additionally, the independence of settling velocities on initial suspension height was verified experimentally at concentrations for which suspension height effects could be expected to occur.

The test column diameter can also influence the settling velocity of a suspension because of hydraulic wall effects and because of the transmission of shear stress from the suspension to the column walls. In this investigation, a column diameter of 4 inches (10.2 cm) together with slow stirring, were assumed to be sufficient to eliminate these effects. Although not verified experimentally, this assumption was considered to be valid because of the column diameter recommendations of Michaels and Bolger (1962). Although column diameter effects have been reported for biological suspensions in columns greater than 4 inches in diameter (Vesilind, 1968a), it must be kept in mind that biological suspensions may represent extreme settling and thickening behavior because of the highly flocculent nature of the microorganisms combined with a very low primary particle buoyant density.

The assumption of uniform size and density of aggregates is consistent with the condition originally assumed in the development of

the basic velocity-voidage correlation upon which Equation (28) is based.

The third and fourth assumptions as listed above are related to the value of the exponent in Equation (28) and they require confirmation upon completion of the analysis.

When Stoke's Law is used to estimate aggregate diameters and densities from the slope and intercept of plots consistent with Equation (28), then it must also be assumed that the aggregates behave as solid spheres and that conditions of creeping flow exist.

Results

The settling velocity versus concentration data were plotted as $v^{1/4.65}$ versus C in Figures 13 and 14. The data of Figure 13 are for high-intensity pretreatment mixing. In Figure 14, high and low pretreatment mixing intensities are compared for polyelectrolyte dosages of 6.25×10^{-5} g/g and 5.00×10^{-4} g/g.

Referring to both Figures 13 and 14, flocculent hindered settling of the suspensions occurred at lower concentrations as evidenced by the linearity of $v^{1/4.65}$ versus C . It is also interesting to note that, at the lower concentrations and for a given pretreatment mixing condition, the effect of suspension concentration on the settling velocity raised to the $1/4.65$ power was independent of the polyelectrolyte dosage as indicated by the approximately equal slopes.

At intermediate concentrations of 60 kg/m^3 to 150 kg/m^3 and polyelectrolyte dosages of 2.50×10^{-4} g/g and greater, the occurrence of channelling is readily identified by the concave-downward nature of

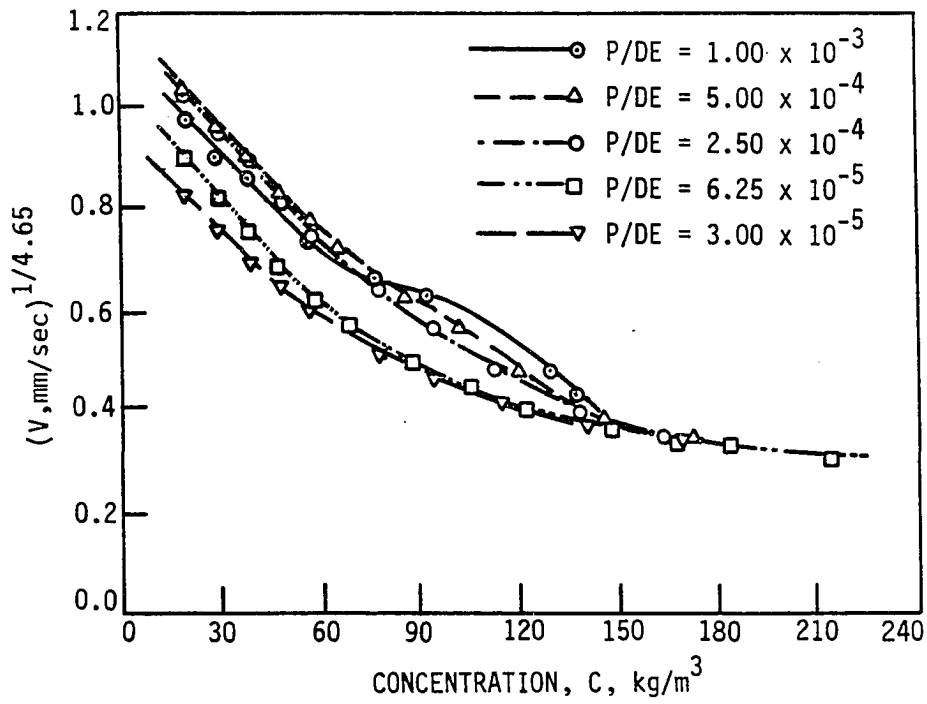


Figure 13. Settling velocity versus suspension concentration plotted according to Equation (28) for various polyelectrolyte dosages and high intensity pretreatment mixing

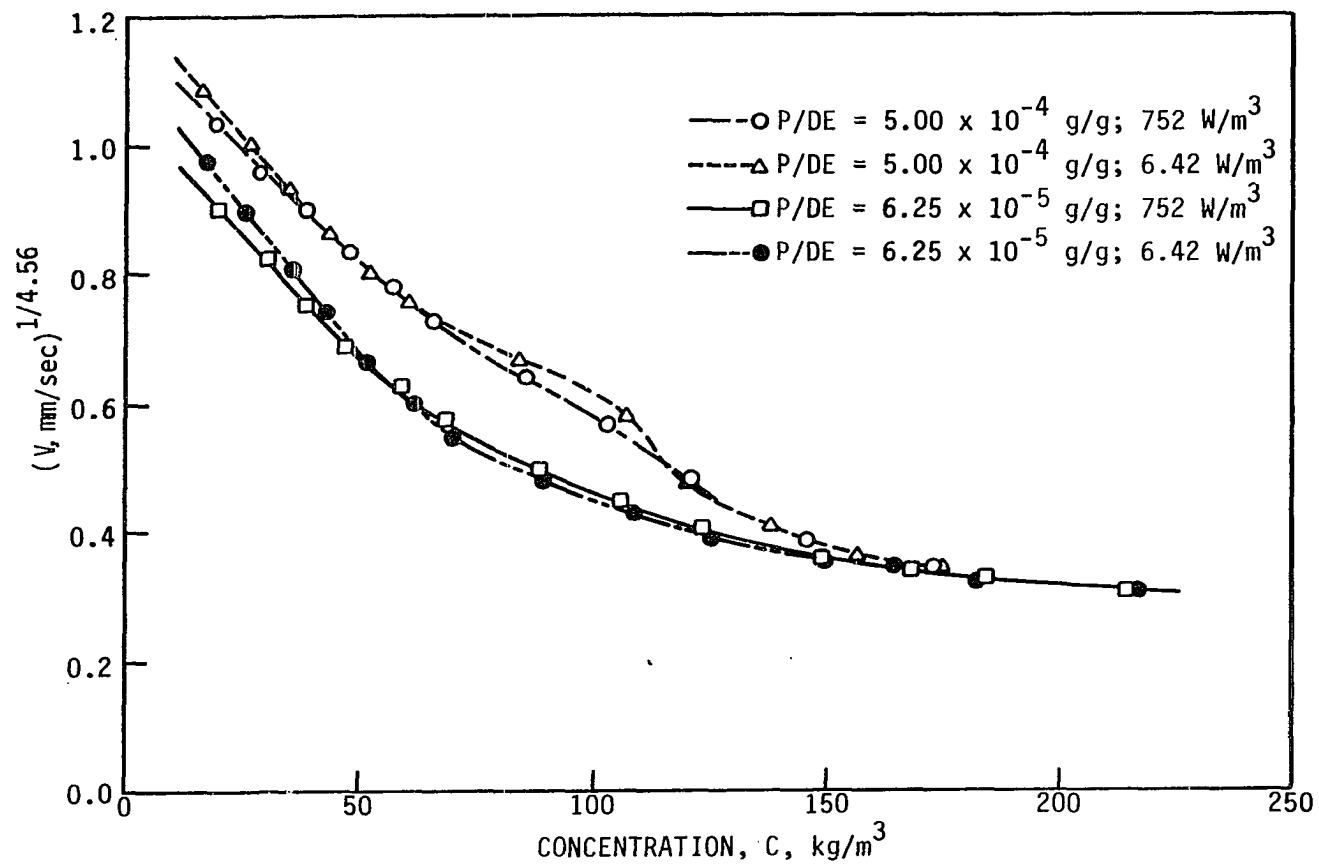


Figure 14. Settling velocity versus suspension concentration plotted according to Equation (28) for high and low intensities of pretreatment mixing at two polyelectrolyte dosages

the corresponding curves in Figures 13 and 14. The severity of the channelling increased with polyelectrolyte dosage and not inversely with the absolute value of the measured suspension zeta potential. The occurrence of channelling was, therefore, related to the bridging type of particle attachment that occurs with long-chain organic molecules rather than strictly a surface charge neutralization phenomenon.

High-intensity pretreatment mixing resulted in less channelling than did low-intensity mixing. This may indicate an effect of mixing intensity which is related to the orientation and distribution of the polyelectrolyte molecules on the surface of the Celite 512 particles.

At polyelectrolyte dosages of 3.00×10^{-5} g/g and 6.25×10^{-5} g/g, the upper limit of flocculent hindered settling was marked by a gradual decrease in slope, and a merging of all settling velocities occurred at the highest concentrations examined regardless of the polyelectrolyte dosage or pretreatment mixing intensity.

Estimation of aggregate properties

Aggregate volume concentrations, diameters, and densities, as functions of concentration, were estimated by applying Equation (28) as proposed by Javaheri and Dick (1969) and illustrated by Figure 15. The slope $-KV_0^{1/4.65}$ of a tangent at any concentration was estimated as the average of the slopes of the point of tangency and the preceding and following data points. Values of K and $KV_0^{1/4.65}$ were then calculated by substituting the estimated slope and the concentration of the point of tangency into Equation (28). From K and $V_0^{1/4.65}$, the aggregate properties of ϕ_a , $(\rho_a - \rho_1)$, and d_a were then readily calculated using

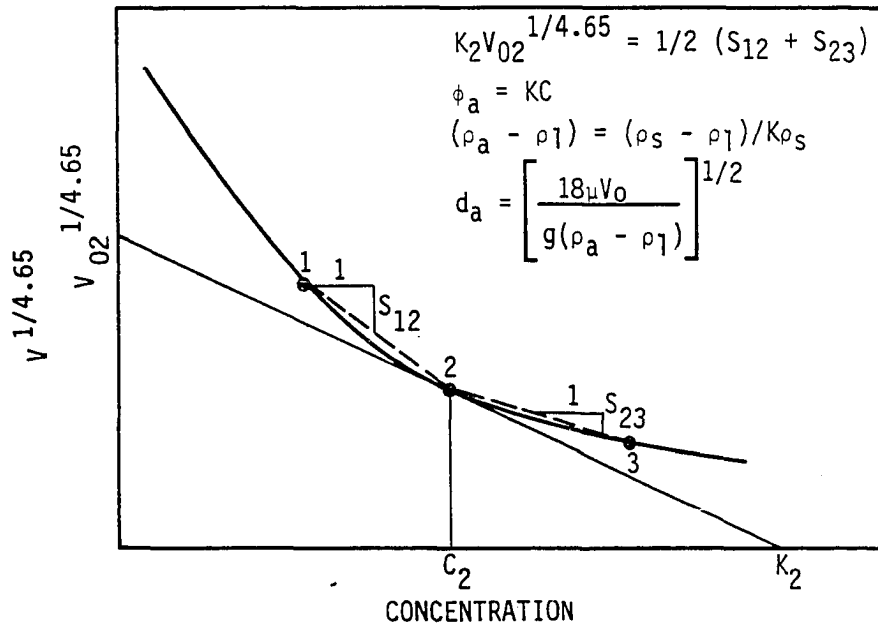


Figure 15. Typical settling velocity versus concentration data plotted according to Equation (28) illustrating the calculations required for estimation of aggregate properties

the equations listed in Figure 15. For all calculations, a temperature of 20°C was assumed.

This procedure was used to estimate the prevailing aggregate characteristics over the initial, linear $v^{1/4.65}$ versus concentration range as well as over the nonlinear range at higher concentrations. The more flocculent suspensions with polyelectrolyte dosages of 2.50×10^{-4} g/g and greater were not subjected to this analysis over the full concentration range because of the effect of channelling on the settling velocities. The results of these analyses are presented in full in the Appendix.

The estimated aggregate volume concentrations for all conditions of polyelectrolyte dosage and pretreatment mixing intensity were plotted versus concentration in Figure 16. At low concentrations, corresponding to the range of flocculent hindered settling of aggregates, the interaggregate porosity, $(1 - \phi_a)$, decreased linearly with increasing concentration at a rate that was approximately independent of the degree of flocculent nature of the suspension and of the pretreatment mixing intensity. At higher concentrations in the absence of channelling, the interaggregate porosities became approximately constant with an average value of 0.65. These two concentration ranges will hereafter be referred to as the "variable" and "constant" interaggregate porosity concentration ranges, respectively.

Over the variable interaggregate porosity range, the estimated aggregate diameter and densities were constant as expected from theory for a given polyelectrolyte dosage and pretreatment mixing intensity.

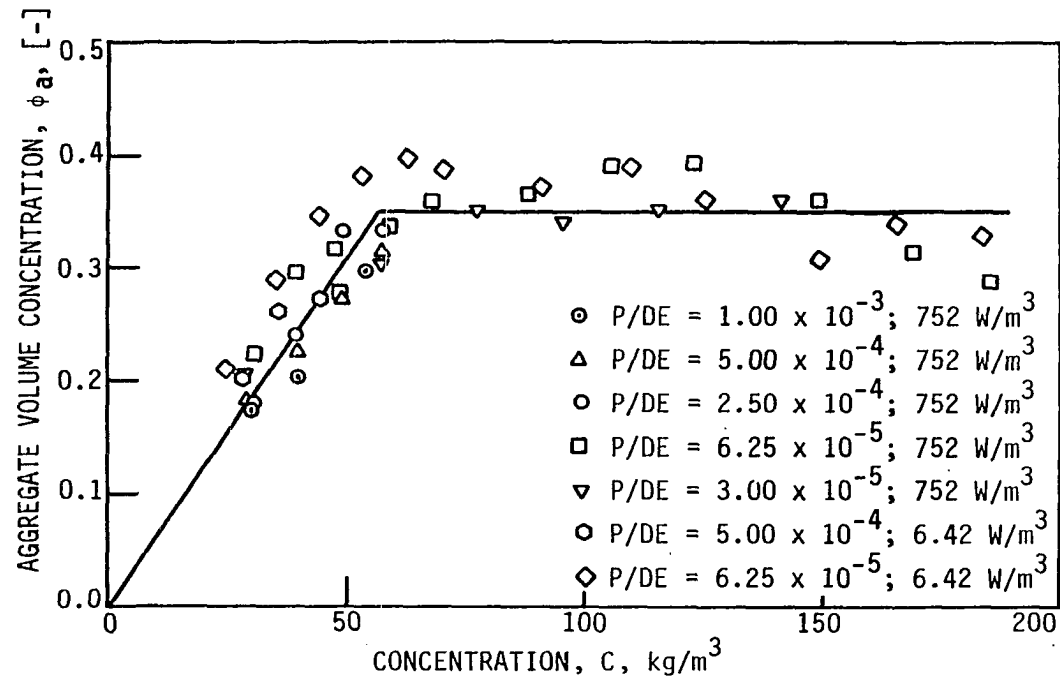


Figure 16. Aggregate volume concentration versus suspension concentration for all conditions of polyelectrolyte dosage and pretreatment mixing intensity

These values are presented in Table 1. The aggregate diameters and densities as a function of polyelectrolyte dosage for high-intensity pretreatment mixing are also illustrated graphically in Figure 17. The maximum aggregate diameter and density for a mixing intensity of 752 W/m^3 did not occur at a polyelectrolyte dosage of 5.00×10^{-4} g/g corresponding to a near-zero suspension zeta potential. The largest aggregate was formed at a lower polyelectrolyte dosage and the aggregate densities increased with polyelectrolyte dosage. Low intensity pretreatment mixing resulted in the formation of much larger, but less dense aggregates. The dependence of aggregate properties on polyelectrolyte dosage and not specifically on the magnitude of particle surface potential, provides additional evidence for the role of polymer

Table 1. Estimated aggregate diameters, densities, and Reynolds numbers for the variable interaggregate porosity concentration range

Polyelectrolyte Dosage (P/DE, g/g)	Pretreatment mixing intensity (W/m^3)	Aggregate diameter (d_a , μm)	Aggregate density (ρ_a , g/cm^3)	Reynolds number (Re)
3.00×10^{-5}	752	134	1.080	0.10
6.25×10^{-5}	752	183	1.072	0.24
6.25×10^{-5}	6.42	219	1.068	0.39
2.50×10^{-4}	752	216	1.087	0.48
5.00×10^{-4}	752	196	1.092	0.39
5.00×10^{-4}	6.42	265	1.074	0.76
1.00×10^{-3}	752	158	1.101	0.22

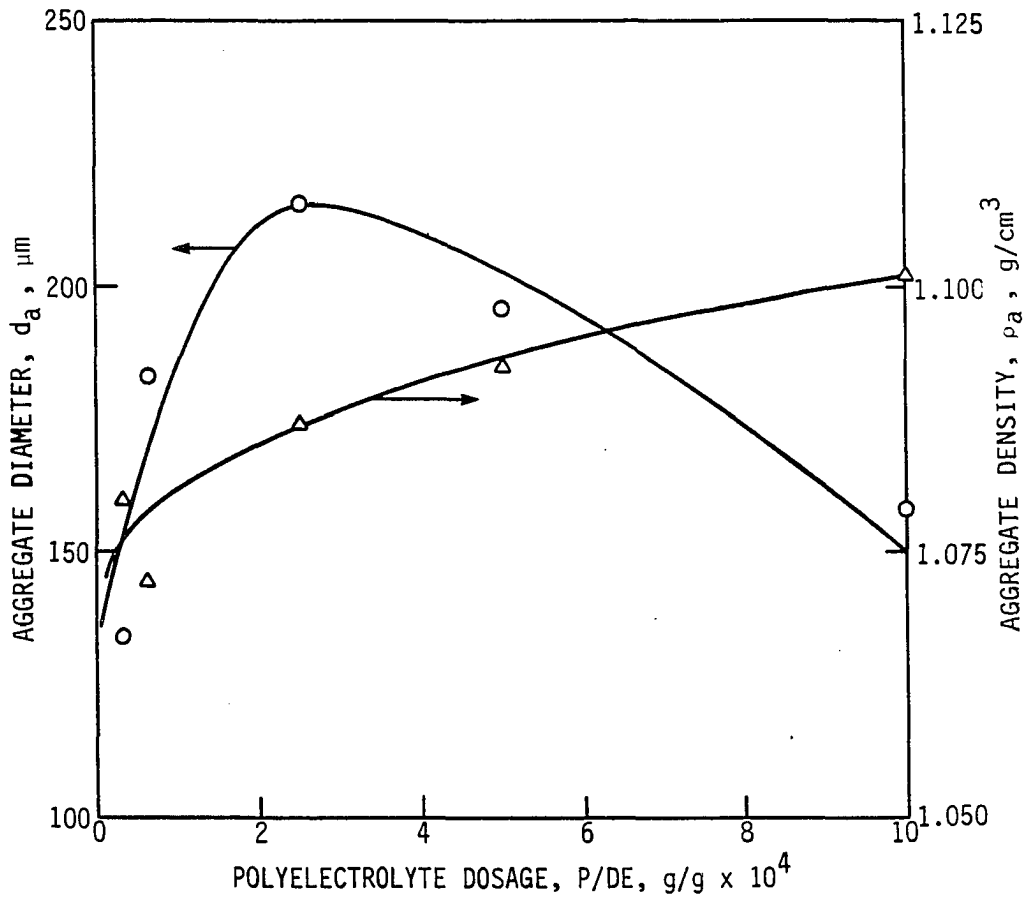


Figure 17. Aggregate diameter and density versus polyelectrolyte dosage for the variable interaggregate porosity range of hindered settling with high-intensity pretreatment mixing

bridging in determining the flocculent nature of these suspensions.

Reynolds numbers based on the estimated aggregate diameters and unhindered settling velocities ranged from 0.10 to 0.76 as listed in Table 1. The assumption of $Re < 0.2$ required for $n = 4.65$, as used in Equation (28), and the assumption of $Re < 0.1$ as is frequently recommended for the use of Stoke's Law, were therefore not valid for the majority of the suspensions at concentrations for which flocculent hindered settling occurred. For those suspensions for which $Re \geq 0.2$, the aggregate estimated diameter and density based on $n = 4.65$ would be expected to be higher and lower, respectively, than estimates obtained by considering n as a function of the Reynolds number (as given by Equations (8) and (9)) as demonstrated by Fouda and Capes (1979).

In order to estimate the errors introduced by making the above assumptions, the data for the polyelectrolyte dosage of 5.00×10^{-4} g/g and low intensity mixing, which represent the worst case with respect to the Reynolds number assumptions, were subjected to a more rigorous analysis.

The four initial data points corresponding to the linear range of $v^{1/4.65}$ versus C were fit to Equation (28) using linear regression analysis and the resulting estimated aggregate parameters were:

$$d_a = 250 \mu\text{m}$$

$$\rho_a = 1.078 \text{ g/cm}^3,$$

$$v_o = 2.63 \text{ mm/sec}$$

$$Re = 0.66$$

where the aggregate diameter was based on Stoke's Law. Regression analysis was used to facilitate these calculations and these parameter estimates therefore differ slightly from the parameters reported in Table 1 which are the average of the parameters estimated for each concentration of the variable interaggregate porosity range.

A new value of n was then calculated using Equation (9) as given by

$$n = (4.35 + 17.5 \frac{d}{D}) \text{Re}^{-0.03} \quad (9)$$

which is applicable for $0.2 \leq \text{Re} \leq 1$ and the result was $n = 4.45$. The four velocity-concentration pairs were then analyzed again using $n = 4.45$.

Above a Reynolds number of 0.1, the drag coefficient, C_D , for a sphere is not equal to $24/\text{Re}$ and Stoke's Law is not valid. A correlation of Re verses C_D/Re as given in Table 5-26 of Perry and Chilton (1973) was used to calculate the Reynolds number from which the aggregate diameter could be estimated. The resulting parameters from this analysis were

$$d_a = 258 \mu\text{m}$$

$$\rho_a = 1.076 \text{ g/cm}^3$$

$$V_o = 2.60 \text{ mm/sec}$$

$$\text{Re} = 0.67$$

and for these values, n was again found to be 4.45. These parameters were, therefore, more correct values than those obtained assuming $n = 4.65$ and using Stoke's Law to calculate the aggregate diameter. The

errors introduced by these assumptions were small, -- d_a was underestimated by 3 percent and ρ_a was over-estimated by 0.2 percent. The assumptions required for the use of Equation (28) and Stoke's Law were therefore considered to be valid based on this rigorous analysis of the worst case. The underestimation of diameter and overestimation of density were, however, opposite of what was expected based on the results of Fouda and Capes (1979), but this discrepancy may have been due to their use of polynomial relations to relate the unhindered settling velocity to Re and the use of the Re versus C_D/Re correlation herein.

Channelling did not occur with polyelectrolyte dosages of 3.00×10^{-5} g/g or 6.25×10^{-5} g/g and aggregate diameters and densities were estimated over the full range of concentrations that were investigated. Reynolds numbers were again calculated to check the validity of the assumptions that were required for the use of Equation (28) and Stoke's Law. For the polyelectrolyte dosage of 3.00×10^{-5} g/g, Re was less than 0.2 for all estimated aggregate diameters. For a dosage of 6.25×10^{-5} g/g, Re was less than 0.2 for all but the largest of the estimated diameters.

The estimated aggregate diameters and corresponding buoyant densities for high intensity pretreatment mixing were plotted logarithmically in Figure 18. As with the data of Javaheri and Dick (1969) and Shin and Dick (1975, 1980) illustrated in Figure 4, the buoyant densities were fit very well by an equation of the form of Equation (23):

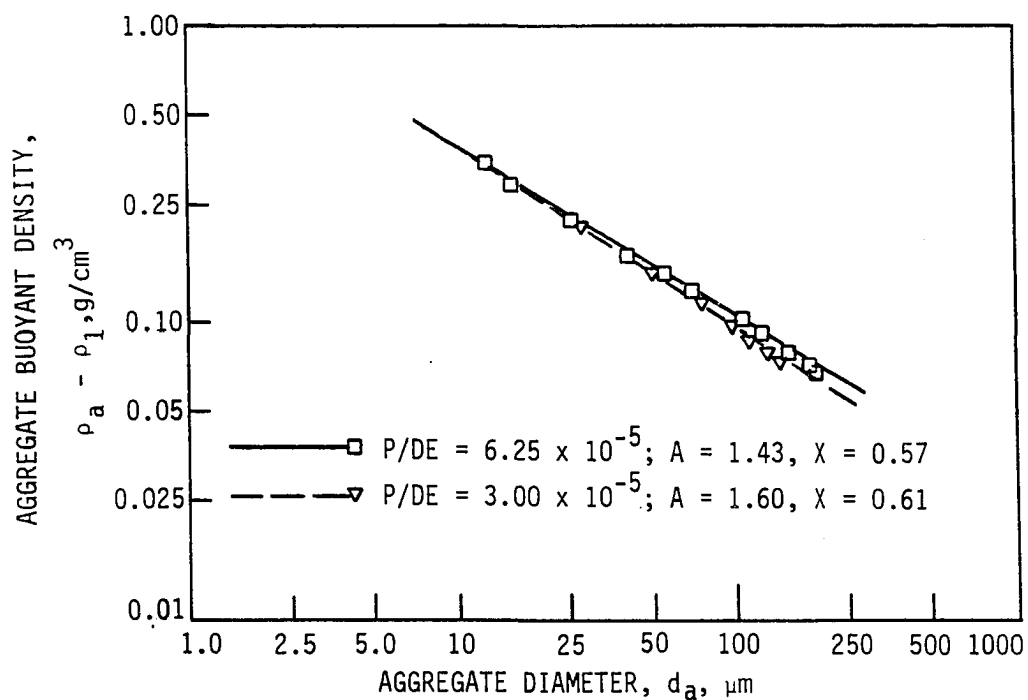


Figure 18. Aggregate buoyant density versus diameter for polyelectrolyte dosages of $3.00 \times 10^{-5} g/g$ and $6.25 \times 10^{-5} g/g$ and high-intensity pretreatment mixing over the constant inter-aggregate porosity range of hindered settling

$$(\rho_a - \rho_l) = A d_a^{-X} \quad (30)$$

where A and X are constants for a given polyelectrolyte dosage as listed in Figure 18. Although not presented in Figure 18 for reasons of clarity, the buoyant density diameter data for low-intensity mixing at a polyelectrolyte dosage of 6.25×10^{-5} g/g varied little from the high-intensity mixing data and the corresponding constants were $A = 1.31$ and $X = 0.55$.

The correlation of the aggregate buoyant density-diameter data by Equation (30) is in agreement with the published experimental and theoretical results of Lagvankar and Gemmell (1968), Matsumoto and Mori (1975), and Tambo and Watanabe (1979) on the characteristics of aggregates of flocs formed by coagulation and flocculation of very dilute particulate systems.

Examination of Figure 18 reveals that the buoyant density-diameter data for the two polyelectrolyte dosages coincide at an aggregate diameter of between 10 and 15 μm . Since the Celite 512 has a reported median particle diameter of 15 μm , then the coincidence of data occurs at the smallest possible aggregate which, of course, is the primary particle.

In comparing Equation (27), that was derived from the work of Thomas (1963) with Equation (30) and setting the exponent of Equation (27) equal to X, the proportionality constant A can be expressed as

$$A = (\rho_p - \rho_l) (d_p)^X \quad (31)$$

from which a Celite 512 particle density of 1.3 g/cm^3 (composite density

of solid material plus intraparticle water) can be calculated for $d_p = 15 \mu\text{m}$ and either of the values of A and X listed in Figure 18. Although the measured density of Celite 512 was 2.17 g/cm^3 , an effective primary particle density of 1.3 g/cm^3 would not be unreasonable considering the angular and porous nature of the skeletal diatoms. That is, a certain amount of immobile water would be associated with the particles and the apparent density of the particle plus immobile water would be less than true density of the solid material of which the particles are composed.

DISCUSSION

Discussion of the procedures, results, and assumptions required for the methods of analysis used in this investigation were included in the initial presentations of those topics and will not be repeated here. There are, however, many aspects of this investigation that require further discussion and development regarding the results and observations of this investigation and their significance and implications with respect to the overall topic of gravity thickening of flocculent suspensions.

General Discussion

The primary data that were obtained in this investigation were the settling velocities of a flocculent suspension as a function of suspension concentration. Five levels of polyelectrolyte dosage representing a wide range of degrees of flocculent nature, and two intensities of pretreatment mixing which differed by an order of magnitude were examined.

Experimental considerations

Obtaining a particulate system which would lend itself to this type of investigation was the subject of a number of preliminary evaluations. The variables of concern were particle size, material availability, the method of controlling the flocculent nature of the particles, and the stability of the chosen system with respect to time-dependent changes in the flocculent nature, as indicated by the zeta potential.

The major obstacle encountered was the effect of suspension

concentration on the ability to maintain a constant zeta potential over the ranges of solids concentrations that were investigated. Initially, it was hoped that the use of organic polyelectrolytes could be avoided because of the possible influence of particle bridging by the long-chain molecules on the settling behavior. Systems of inorganic coagulants with dosages that were proportional to the suspension concentration exhibited a strong dependence of supernatant pH and particle zeta potential on suspension concentration and were eliminated from further consideration.

The influence of suspension concentration on zeta potential at a constant flocculent dosage was not entirely eliminated by using the Cat Floc-T-Celite 512 system, as was illustrated in Figures 7 and 8. The measured zeta potentials were, however, stable with respect to time and pretreatment mixing intensity.

Regardless of the variation of zeta potential with suspension concentration, the results of this investigation were not adversely affected. At low suspension concentrations, the zeta potentials were nearly constant and the results and analysis of the variable interaggregate porosity range of settling would be unaffected. At higher concentrations, only the results for the lowest two polyelectrolyte dosages, which exhibited the least dependence of zeta potential on suspension concentration, were analyzed because of channelling within the more flocculent suspensions. For the highest suspension concentrations that were examined, the most significant result was the apparent independence of the settling velocity on both

the polyelectrolyte dosage and pretreatment mixing intensity. This result, again, was unaffected by the changes in zeta potential with concentration because at these concentrations, a range of zeta potentials of -40 mV to about 0 mV was represented by the data.

Settling velocity as a function of concentration

Much of the work involving batch settling or thickening reported in the literature has been conducted under experimental conditions for which the observed settling velocities may have been functions of variables other than concentration. The experimental conditions and procedures of this investigation were such that the observed settling velocities were a function of concentration only. This was insured by using a stirred, 4-inch diameter batch settling column and measuring the initial rate of interface subsidence. Additionally, the settling velocities at intermediate and higher concentrations were found to be independent of initial suspension height.

The independence of suspension settling velocity from initial suspension height for low concentrations, corresponding to the variable interaggregate porosity range of settling identified in this investigation, is well-documented in the literature. At higher concentrations, suspension height effects can arise from two phenomena. At intermediate concentrations, over which substantial channelling and structural integrity of the suspension can occur, initial suspension height effects on the observed interface subsidence velocity can arise because of the rate process nature of channel formation and because of the support of the interface that can be transmitted from underlying

solids through networks of particle-particle contacts. At high concentrations, the existence of intraparticle pressure is of major importance.

The independence of settling velocities of the polyelectrolyte-coated particulate system of this investigation, from initial suspension height effects, indicated that solids pressure, and therefore compression of the aggregate structures, did not exist in the vicinity of the subsiding interface. As was shown by Shirato et al. (1970), at very high concentrations, concentration-only-dependent settling occurs only in the absence of compressive forces. As a result, concepts of the nature and role of aggregate formation in gravity thickening that will be presented later will differ significantly from the ideas that have been expressed by other researchers who have assumed that compression of the aggregate structures which form during the settling of flocculent suspensions is a major factor which governs the size and density of the aggregates that exist at intermediate and higher concentrations.

Estimation of aggregate characteristics

Using the primary data of settling velocity as a function of concentration, the sizes and densities of the aggregates which formed during the settling process were estimated using a velocity-voidage correlation for the hindered settling of spheres that had been previously applied to the batch settling of flocculent suspensions by other researchers. A discussion and evaluation of the assumptions that were required for the analysis has already been presented and will not be repeated here. The implication of the assumption that the aggregates

behaved as solid spheres, however, merits additional consideration.

Taken at face value, the assumption that the aggregates were solid spheres would obviously be in error. Aggregates of primary particles can be voluminous structures which contain a significant amount of water. Additionally, photographic evidence and theoretical flocculation simulations indicate that the aggregates that form during settling are probably angular in nature. As an aggregate settles, then, a certain amount of intraaggregate flows could be expected. Intraaggregate flow during settling was felt by Matsumoto et al. (1980) to be a significant factor in the settling of activated sludge which resulted in settling velocities for equivalent diameter permeable aggregates which were greater than would be expected for impermeable aggregates. On the other hand Thomas (1963) reported that the ratio of internal to external flow for the particulate systems that he investigated was always less than 5 percent.

The angular, nonuniform shape of an aggregate would result in a lower settling velocity than would be expected for a sphere of equal volume because of an increase in the drag coefficient of Equation (1) over that of a sphere. This was taken into account in the work of Tambo and Watanabe (1979) who assumed an aggregate sphericity (surface area of equivalent volume sphere divided by actual surface area) of 0.8 which resulted in a slightly less than twofold increase in the drag coefficient and therefore the estimated aggregate buoyant densities were about one-half of the value that would have been obtained in their investigation if the assumption of spheres were to have been made.

Also, the correct value of n for nonspherical settling bodies may be greater than the value of 4.65 that was used herein (Chong et al., 1979).

The effects of intraaggregate flow and nonspherical aggregate shape have the potential to significantly affect the results of an investigation such as that reported herein. It should be emphasized, then, that the estimated aggregate properties based on the assumptions of this investigation, are equivalent spherical properties. That is, a suspension at a given concentration behaved as though it were composed of spherical, impermeable aggregates of a given size or density. At this stage of the development of the concepts reported herein, this is acceptable because, the results will be used to make inferences about the role of aggregate formation in gravity thickening and the estimated aggregate parameters and results will not be used for extrapolation to other particulate systems.

Significant discrepancies could occur as a result of assuming solid, spherical aggregates in, for example, attempts to experimentally verify the aggregate diameters estimated from hindered settling velocity. Michaels and Bolger (1962) and Matsumoto et al. (1980) noted that observed aggregate diameters were greater than the corresponding equivalent spherical, or hydrodynamic, diameters based on settling velocity measurements. In this investigation, the verification of estimated aggregate diameters by observation and measurement was not attempted. Although particle aggregation or flocculation was readily observed as the suspensions settled, the motion of the aggregates would

have prevented accurate measurements. A logical procedure would have been to document the aggregate structure photographically through the column wall from which detailed measurements and observations could have been made. Several problems would have been associated with this procedure--not the least of which would have been the conflict between the short exposure time required because of aggregate motion and the typically long exposure time required for photomicroscopy.

The strongest evidence for the validity of the aggregate diameter and density estimates of this investigation given the assumption of solid, spherical aggregates, then, is the resulting aggregate diameter-density relationships and their agreement with the theoretical and experimental relationships of a variety of particulate systems determined by other researchers.

Role of Aggregate Formation During Batch Settling

The batch settling behavior of the polyelectrolyte coated Celite 512 used in this investigation was characterized by two distinct ranges of interaggregate porosity behavior. At low suspension concentrations. The aggregate volume concentration increased linearly with concentration as illustrated by Figure 16. Conversely, the interaggregate porosity decreased linearly with increasing concentration. This variable interaggregate porosity mode of settling was characterized by the hindered settling of aggregates whose size and density were independent of suspension concentration. At intermediate and higher concentrations, and in the absence of channelling related phenomena, the aggregate volume concentration and, therefore, the

interaggregate porosity remained constant and independent of suspension concentration. This constant interaggregate porosity mode of settling was characterized by hindered settling of aggregates whose size and density varied with concentration as required to maintain the constant interaggregate porosity. Two distinct modes of variable and constant, or nearly constant, interaggregate porosity settling are also evidenced by the results presented by Javaheri and Dick (1968) and Shin and Dick (1980). Additionally, the size and density of the aggregates which form are related by the basic structure of the aggregates.

Variable interaggregate porosity settling

As a flocculent suspension is introduced into a batch settling column, any preexisting flocs, aggregates, or structure may be destroyed and, upon the attainment of quiescent conditions, re-aggregation of the suspension will occur. In this investigation, suspensions subjected to both high and low pretreatment mixing intensities, when transferred into the test column, appeared homogeneous. Upon dissipation of the residual fluid motion, however, aggregate structures were readily observed.

Since the aggregation process occurs in the settling column, the factor which limits the size to which the aggregates grow must be a mechanism that exists within the settling column and not the prior conditions of suspension agitation. Other workers have demonstrated that for repetitive tests conducted on the same suspension, effects of pretreatment mixing could be nonexistent or, if present, the effects were reversible (Michaels and Bolger, 1962; Pearse, 1980).

It would be reasonable to assume that the mechanism which limits

the growth of aggregates must be the fluid shear forces that are generated as the aggregates settle. After introduction into a settling column and after the residual fluid motion begins to dissipate, a flocculent suspension will begin to aggregate because of the induced and random motions of the primary particles. As a result of the very high number concentration of particles, the aggregation process would be rapid and the aggregates would begin to settle at a rate which would increase with increasing diameter. During aggregate growth, the aggregate diameter-density relationship would hold and the actual situation would most likely be unsteady-state settling; however, when steady-state is assumed and a typical aggregate size-density relationship as given by Equation (30) with $X < 2$ is combined with Stoke's Law, the result is an increase in settling velocity with increasing aggregate diameter in spite of the corresponding decrease in density.

As aggregate growth proceeds and the settling velocity increases, fluid shear would also increase until a diameter of aggregate is attained such that the yield stress of the surface of the aggregate is equal to the fluid shear stress that would tend to strip particles from the surface and no further net aggregate growth could occur.

The concept of velocity gradient, or more precisely the root-mean-square velocity gradient, has been found to be a variable that can limit the growth of aggregates in very dilute systems. An analysis of the velocity gradients occurring within fluidized beds has been used to examine flocculation in the interstices of a fluidized bed (Ives and Al

Dibouni, 1979) and as a tool for analyzing the effectiveness of the filter backwashing process (Valencia and Cleasby, 1979). The velocity gradient for a fluidized bed or a mass of settling particles is a function of the porosity and therefore would be untenable as the mechanism that limits the aggregate size in variable interaggregate porosity settling because in such systems the aggregate size and density are constant over a wide range of concentrations.

A basic premise of the analysis of Richardson and Zaki (1954) was that the resistance force acting on the individual particles remained constant and were independent of concentration or porosity. The resistance force is the sum of the form and friction drag forces acting on the particle. In a discussion of creeping flow around a sphere, Bird et al. (1960) presented an expression for the shear stress acting at any point on the surface of a sphere. The maximum shear stress occurs at the circumference of the sphere which is normal to the direction of flow past the sphere. For an aggregate whose settling velocity is given by Stoke's Law, the maximum shear stress, τ_{\max} , would be given by

$$\tau_{\max} = \frac{g(\rho_a - \rho_l)d_a}{6} \quad (32)$$

For an aggregate size density relationship such as Equation (30) with the exponent X less than one, the maximum shear stress acting at the surface is independent of concentration and increases with increasing diameter.

The strengths of aggregates or flocs have been found to be, as with

buoyant density, inversely proportional to the diameter raised to some power and, therefore, decreasing with increasing diameter (Matsuo and Unno, 1981). This would be expected since the number density of primary particles, and therefore the number of particle-particle bonds, decreases with radial distance outward from the center of the aggregate.

Variable interaggregate porosity settling that occurs with dilute, flocculent suspensions can therefore be characterized by the growth of aggregates or flocs to some size at which the fluid shear stress that tends to strip particles from the extremities of the aggregate is equal to the yield stress of the aggregate structure at the prevailing diameter. The size of aggregate which occurs for a given system is independent of concentration and the effect of concentration on the hindered settling velocity is simply one related to the number concentration of aggregates and the effective suspension porosity.

Constant interaggregate porosity settling

As the concentration of a dilute, flocculent suspension is increased, the interaggregate porosity decreases to a point at which, upon an additional increase in concentration, interaggregate contact would occur if the aggregate size and density were to remain constant. In this investigation, and in those of other researchers, the upper concentration limit of variable interaggregate porosity settling, in the absence of channelling related phenomena, was marked by a distinct change in the dependence of interaggregate porosity on concentration from a proportional relationship to a relatively constant interaggregate porosity. The onset of the constant interaggregate porosities were also

accompanied by a dependence of aggregate size and density on concentration.

The aggregates which form over the constant interaggregate porosity concentration range undergo hydrodynamically hindered settling as evidenced by the dependence of settling velocity on the concentration only for the particulate system of this investigation.

Based on the previous discussion of aggregate strength and fluid shear forces, the smaller aggregates formed would have strengths which would exceed the prevailing fluid shear stresses and an alternate mechanism must limit the size to which aggregates can grow. This mechanism would most likely be abrasion of aggregates due to collisions between the aggregates as they rotate and move throughout the suspension. At this point it is interesting to note that aggregate movement occurred within the settling bed that was similar to, but not as intense as, the large-scale streaming of particles that is observed during fluidization operations.

The relatively constant interaggregate porosity that is maintained independent of concentration could be expected to be similar in nature to the porosity of minimum fluidization velocity. That is, the constant interaggregate porosity is the minimum interaggregate porosity at which the motion of individual aggregates is not restricted. For this investigation, the minimum interaggregate porosity was approximately 0.65. The average minimum interaggregate porosities for the data of Javaheri and Dick (1969) and Shin and Dick (1980) were both about 0.6. These porosities are somewhat greater than typical minimum fluidization

porosities for spherical, or nearly spherical particles (Cleasby and Fan, 1981), but they may represent some percentage increase over the minimum theoretical interaggregate porosity so that lasting interaggregate contact does not occur.

For the more flocculent suspensions of this investigation, constant interaggregate porosity settling was precluded by channelling related phenomena. At these higher polyelectrolyte dosages, a certain amount of interaggregate attachment existed within the suspension possibly because the aggregate strengths were greater than the mechanical abrasion stresses within the suspension.

It has been said that the porosity remained constant, or nearly so. Upon examination of Figure 16, the interaggregate porosities for this mode of settling tended to increase somewhat with increasing concentration. A possible explanation of this behavior can be put forth based on the effect of particle sphericity on the minimum fluidization porosity which increases with decreasing particle sphericity (Cleasby and Fan, 1981). The slight increase in interaggregate porosity with increasing concentration evident in Figure 16 could have been the result of a decrease in the sphericity of the aggregates with decreasing aggregate size since the smallest aggregates composed of only a few primary particles would take on the angular characteristics of the skeletal diatoms. The minimum interaggregate porosities estimated for a calcium carbonate suspension (Shin and Dick, 1980) and an activated sludge (Javaheri and Dick, 1969) decreased with increasing concentration and, similarly, could be explained by an increase in sphericity with

decreasing diameter because of the more spherical primary particle morphology that would be expected for those types of suspensions.

Over the constant interaggregate porosity mode of settling, the dependence of settling velocity on concentrations is a result of the indirect effect of concentration on aggregate diameter, which is required for the maintenance of the minimum interaggregate porosity. This is reflected through a decrease in V_0 with increasing suspension concentration. An upper concentration limit exists, however, for this mode of settling and corresponds to the concentration at which the aggregate diameter equals that of the primary particles of the suspension.

At still higher concentrations, the settling of a flocculent suspension would be expected to revert to variable porosity settling as governed by the primary particle diameter and density and as given by Equation (28). Such behavior is evidenced by the results of Scott (1968a).

Aggregate diameter-density relationship

As previously mentioned, the form of the aggregate diameter-density relationships that were obtained for polyelectrolyte dosages of 3.00×10^{-5} g/g and 6.25×10^{-5} g/g were in agreement with those derived from the settling data of other researchers that were illustrated in Figure 4 as well as with the additional theoretical and experimental relationships that were cited.

Aggregate diameter-density relationships can also be estimated for the remaining polyelectrolyte dosages for tests in which channelling

occurred. The parameters A and X of Equation (30) can be estimated from the two known aggregate sizes and densities of each polyelectrolyte dosage: the size and density of the aggregates formed over the variable interaggregate porosity range and the size and effective density of the primary particles of the suspension. This has been done and the results are reported in Table 2 along with the previously reported values for polyelectrolyte dosages of 3.00×10^{-5} g/g and 6.25×10^{-5} g/g.

Table 2. Values of A and X for the aggregate diameter-density relationship Equation (30), for all conditions of polyelectrolyte dosage and pretreatment mixing intensity

Polyelectrolyte dosage (P/DE, g/g)	Pretreatment mixing intensity (W/m ³)	Constants of Equation (30)	
		A, g/cm ³	X
1.00×10^{-3}	752	1.05	0.46
5.00×10^{-4}	752	1.04	0.46
5.00×10^{-4}	6.42	1.12	0.48
2.50×10^{-4}	752	1.05	0.46
6.25×10^{-5}	752	1.43	0.57
6.25×10^{-5}	6.42	1.31	0.55
3.00×10^{-5}	752	1.60	0.61

The relationship between the size and density of the aggregates of a settling suspension plays a fundamental role in determining the settling velocity of the suspension. Over the low concentration, variable interaggregate porosity range of hindered settling, the

aggregate size and density govern the fluid shear forces and the strength of the aggregate which limits the size of the aggregate and, in turn dictates the hindered settling velocity of the suspension at any given concentration. With the intermediate and higher concentrations in constant interaggregate porosity settling, the aggregate diameter-density relationship directly controls the dependence of the hindered settling velocity on concentration through the unhindered settling velocity of the aggregates.

In the discussion of the fluid-shear-limited growth of aggregates at lower suspension concentrations, a condition of $X < 1$ was imposed for the calculation of shear stress by Equation (32). A condition of $X < 2$ was also imposed to ensure that the unhindered settling velocity of an aggregate increases with increasing diameter. The criterion of $X < 2$ may be a general condition valid for all types of flocculent suspensions. For the particulate systems investigated by Tambo and Watanabe (1979), however, diameter exponents of $X = 1.4$ were reported. This was believed to be characteristic of a structure which consisted of a cluster of individual aggregates which occurred for larger estimated aggregate diameters. A similar, secondary type of structure was discussed by Lagvankar and Gemmell (1968). The observed secondary structures were, however, formed under various conditions of mixing and, therefore, may not occur in a settling suspension.

Effects of Polyelectrolyte Dosage and Pretreatment Mixing Intensity

The effects of the polyelectrolyte dosage and the pretreatment mixing intensities on the settling characteristics of the Celite 512 suspensions used in this investigation can be accounted for by considering their effects on the aggregate diameter-density relationship and on the strength of the aggregates.

Effect of polyelectrolyte dosage

The polyelectrolyte dosage affected both the strength of the aggregates which formed and the aggregate diameter-density relationship. Upon examination of the exponents Equation (30) presented in Table 2, a trend of decreasing X with increasing polyelectrolyte dosage is evident. In terms of the structure of the aggregates, this would indicate that for the more flocculent polyelectrolyte dosages, a larger number-density of primary particles and less void space existed at any given increment of aggregate diameter than for a lower polyelectrolyte dosage. The variation in the values of A listed in Table 2 are of little significance because they themselves are functions of X as given by Equation (31).

The characteristics of the aggregates which formed over the variable interaggregate porosity range of settling were illustrated in Figure 17. The aggregate densities increased with polyelectrolyte dosage while the aggregate diameter reached a maximum at a dosage of 2.50×10^{-4} g/g and decreased thereafter. The maximum fluid shear stress as given by Equation (32) can be assumed to be the shear strength

of the surface of the aggregates which form during variable interaggregate porosity settling. Based on this assumption, the aggregate yield stresses as a function of polyelectrolyte dosage can be and were calculated and are listed in Table 3. In general, the yield stress of the surfaces of the aggregates increased with polyelectrolyte dosage and then decreased as the polyelectrolyte dosage was increased beyond 5.00×10^{-4} g/g which corresponded to a near zero zeta potential. Although the maximum yield stress for a pretreatment mixing intensity of 752 W/m^3 occurred at a polyelectrolyte dosage of 2.50×10^{-4} g/g and was $0.01 \text{ g/cm} \cdot \text{sec}^2$ greater than the value for a dosage of 5.00×10^{-4} g/g, neither this difference, nor the implication of a maximum yield stress at this lower dosage, is considered to be significant.

Table 3. Aggregate yield stress for all conditions of polyelectrolyte dosage and pretreatment mixing intensity

Polyelectrolyte dosage (P/DE, g/g)	Pretreatment mixing intensity (W/m^3)	Aggregate yield stress (τ_y , g/cm sec^2)
1.00×10^{-3}	752	0.26
5.00×10^{-4}	752	0.30
5.00×10^{-4}	6.42	0.32
2.50×10^{-4}	752	0.31
6.25×10^{-5}	752	0.22
6.25×10^{-5}	6.42	0.24
3.00×10^{-5}	752	0.17

Effect of pretreatment mixing intensity

The primary influence of the intensity of pretreatment mixing was related to the orientation of the polyelectrolyte molecules on the surface of the primary particles.

Based on the observations of this investigation and those reported by other researchers, mixing prior to the introduction of a flocculent suspension into a batch settling column was reasoned to have no direct effect on the size and density of the resulting aggregates. This was indicated by the fact that pretreatment mixing intensity had very little effect on the aggregate diameter-density relationship at a polyelectrolyte dosage of 6.25×10^{-5} g/g. The settling velocities of suspensions of low and intermediate concentration were, however, significantly affected by the intensity of mixing.

At a polyelectrolyte dosage of 5.00×10^{-4} g/g with intermediate concentrations, channelling occurred within the suspension and the channelling was more pronounced for a low intensity of pretreatment mixing of 6.42 W/m^3 than for high intensity mixing at 752 W/m^3 . At the lower concentrations of variable interaggregate porosity settling, low-intensity mixing resulted in the formation of larger, less dense aggregates whose hindered settling velocities were significantly greater than for high intensity mixing. Also, the estimated aggregate yield stresses in Table 3 were greater for low-intensity mixing. In view of the lack of effect on the aggregate diameter-density relationship, then, the effects of mixing intensity noted above point to a situation in which high-intensity mixing resulted in a compact and uniform

arrangement of the polyelectrolyte molecules on the primary particles while low intensity mixing allowed for a less uniform coating and the extension of segments of the polymer molecules out into the surrounding liquid. The extended polymer segments could have been available for attachment, and, hence, bridging to another particle. It would also be possible that shearing of the polyelectrolyte molecules could have occurred during the high-intensity mixing.

Based on the relative differences between the values for the aggregate diameter-density relationships reported in Table 2, it could be said that the mixing intensity had an effect on the basic structure of the aggregate that was at least as significant as the effect of the dosage of polyelectrolyte. This argument can be countered, however, by a reexamination of Figure 14 in which the settling velocities for both pretreatment mixing intensities and two polyelectrolyte dosages are compared. First, at a polyelectrolyte dosage of 6.25×10^{-5} g/g, over the range of constant interaggregate porosity settling for which the effect of concentration on settling velocity is a direct result of the aggregate diameter-density relationship, the high and low intensity data agree quite well. Second, over the low concentration range, the high, and low mixing intensity velocities converge at the upper concentration limit of the linear range of $v^{1/4.65}$ versus C. This is similar to the convergence of two tangents to a curve whose points of tangency are separated only slightly. And, this is actually what is represented by the low polyelectrolyte dosage curves of Figure 14. A curve of $v^{1/4.65}$ versus concentration could be constructed based on some aggregate

diameter-density relationship and a constant interaggregate porosity without regard to upper and lower concentration limits. A tangent drawn from any point and extending toward the ordinate axis would represent variable interaggregate porosity settling for the size and density of the aggregates that are characteristic of the point of tangency. The size and density of the aggregates and therefore the point of tangency would, of course, be governed by the strength of the aggregates with respect to the fluid shear forces experienced during settling. A slightly stronger aggregate could withstand variable interaggregate porosity settling at a larger diameter and the point of tangency would, therefore, be displaced upward and the tangent line would have a more negative slope. This is precisely the effect of mixing intensity on settling that was observed in this investigation.

Settling Velocity Correlations

As previously noted in the literature review, there are currently no velocity-voidage correlations which are applicable to the batch settling of a flocculent suspension over a wide range of suspension concentrations. Based on the results of this investigation, this is to be expected because two distinct modes of hindered settling, variable and constant interaggregate porosity settling, can be expected to occur depending on the concentration and degree of flocculent nature of the suspension. For each mode of settling, however, the settling velocities of a flocculent suspension can readily be correlated with interaggregate porosity or suspension concentration.

Over the low concentration, variable interaggregate porosity mode

of settling, any of the velocity-voidage correlations that have been developed for nonflocculent hindered settling can be applied provided that the interaggregate porosity, and not the overall suspension porosity, is used. However, the interaggregate porosity of a flocculent suspension is generally an unknown function of concentration. In order to correlate settling velocity with suspension concentration, then, the velocity-voidage correlation of Richardson and Zaki (1954) expressed in terms of the aggregate properties as given by Equation (28), or other readily modified correlation, must be used.

For constant interaggregate porosity hindered settling in the absence of channelling and compressive phenomena, a simplified settling velocity-concentration correlation can be obtained. For a constant, minimum interaggregate porosity (or maximum aggregate volume concentration, ϕ_{amax}), Equation (15) becomes:

$$V = V_o (1 - \phi_{amax})^{4.65} \quad (33)$$

Then, by making the appropriate substitutions and using Equations (20), (30), and (33), the result is:

$$V = \frac{g}{18\mu} A^{2/X} \left[\frac{(\rho_s - \rho_l)}{(\phi_{amax})\rho_s} \right]^{1-2/X} (1 - \phi_{amax})^{4.65} C^{1-2/X} \quad (34)$$

where all variables are as previously defined. For a suspension of a given flocculent nature, e.g., a given polyelectrolyte dosage, the only variable in Equation (34) is the suspension concentration and the settling velocity can be expressed as:

$$V = \alpha C^\beta \quad (35)$$

where α and β are constants which are functions of the aggregate diameter density relationship, the liquid and solid properties, and the minimum interaggregate porosity of the suspension.

The application of Equations (15) and (35) to the settling velocity data of this investigation is illustrated by Figure 19 which is a plot of solids flux (concentration times settling velocity) versus suspension concentration for polyelectrolyte dosages of 6.25×10^{-5} g/g and 5.00×10^{-4} g/g and high intensity pretreatment mixing. For aggregate volume concentrations of less than 0.35, the dashed curves represent Equation (15) multiplied by C for values of V_o and K as determined by regression analysis of the data expressed as $V^{1/4.65}$ versus C . For constant, maximum aggregate volume concentrations, α and β were calculated from the values of A and X presented in Table 2 and the known liquid and solid properties. Equation (35) was then multiplied by C to obtain the solids flux and is represented by the solid lines of Figure 19.

The parameters α and β for the polyelectrolyte dosage of 6.25×10^{-5} g/g could alternatively have been determined by linear regression analysis of the settling velocity data when expressed as $\log V$ versus $\log C$. This would, however, not be appropriate for the data of the higher polyelectrolyte dosage because of the influence of channelling on the settling velocities. The solid curve for a polyelectrolyte dosage of 5.00×10^{-4} g/g therefore represents the settling velocity behavior

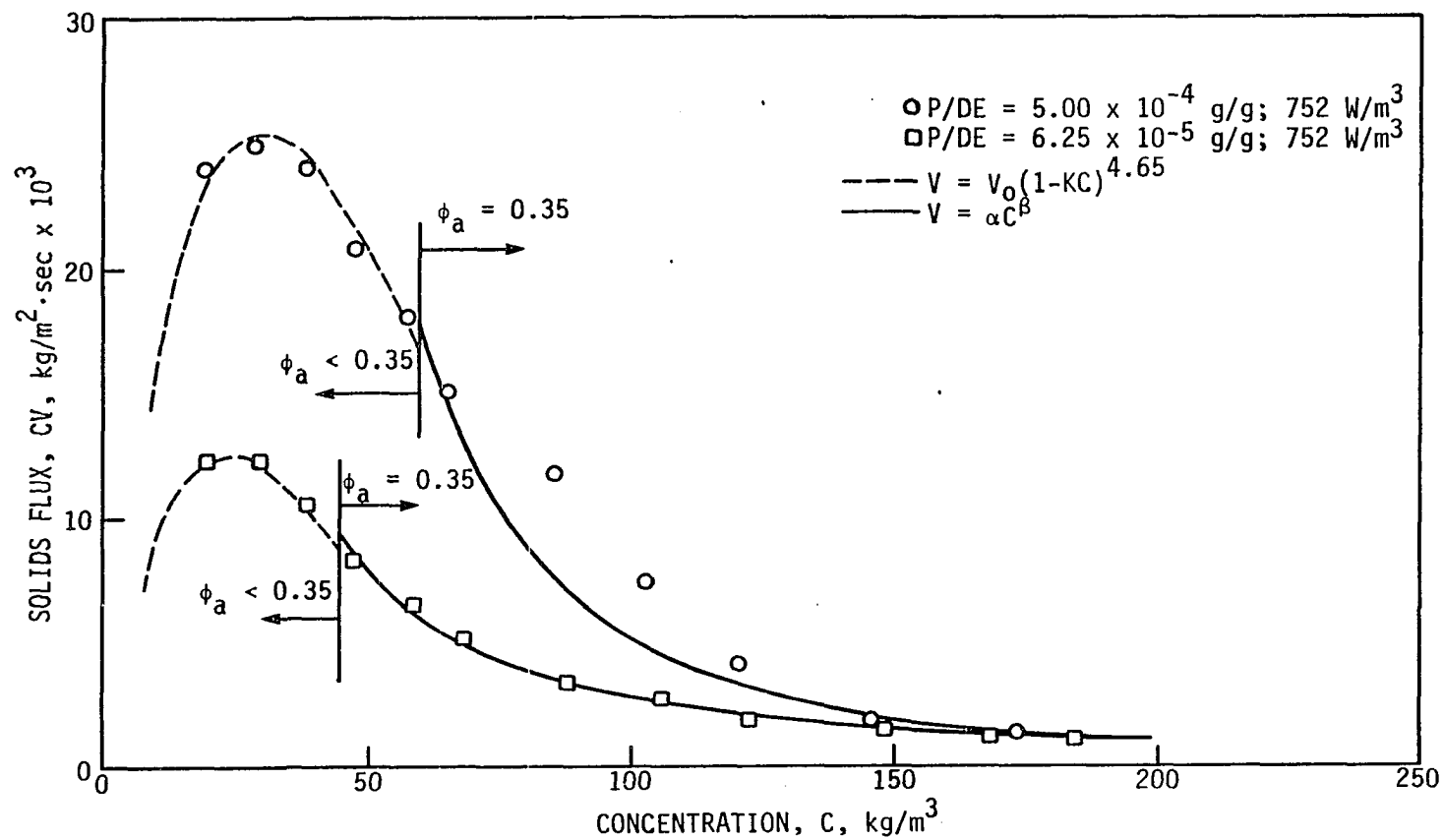


Figure 19. Solids flux versus concentration, for two polyelectrolyte dosages and high-intensity pretreatment mixing, illustrating the variable and constant interaggregate porosity concentration ranges of hindered settling

of the suspension that would be expected if channelling were not to have occurred.

Equation (35) is identical to Equation (18) which was presented as an empirical velocity-concentration correlation that had frequently been applied to the settling of flocculent suspensions in the literature. It is now apparent, however, that the use of this expression does have a sound, theoretical basis provided that the observed settling velocities represent constant interaggregate porosity settling.

SUMMARY AND CONCLUSIONS

Batch settling tests were conducted on a laboratory-prepared, flocculent suspension that consisted of diatomaceous earth coated with an organic, cationic polyelectrolyte. The objectives of the tests were to examine the effects of the degree of the flocculent nature of the suspension, and the intensity of suspension agitation prior to settling on the settling behavior of the suspension, and to quantify the results with respect to the characteristics of the aggregates that formed during the settling process.

The initial settling velocities of the suspensions as a function of suspension concentration were measured and then analyzed using a velocity-voidage correlation in order to estimate the aggregate properties of volume concentration, diameter, and density.

Two distinct modes of hindered settling were observed. At the lower suspension concentrations, the suspensions underwent hindered settling as an assemblage of aggregates whose size and density were independent of concentration. The effect of suspension concentration on the hindered settling velocity was the result of a dependence of the interaggregate porosity on concentration. This mode of settling was termed "variable interaggregate porosity settling." At intermediate and higher concentrations, and in the absence of the formation of channels within the suspension, the suspensions underwent hindered settling as an assemblage of aggregates whose size and density changed such that a "constant interaggregate porosity" was maintained. Additionally, the size and density of the aggregates that formed during constant

interaggregate porosity settling obeyed a relationship that was governed by the physical structure of the aggregates.

Effects of polyelectrolyte dosage and pretreatment mixing intensity were observed only for suspension of low and intermediate concentration. At low suspension concentrations, the suspension settling velocity increased with polyelectrolyte dosage, and therefore suspension zeta potential to a maximum settling velocity which corresponded to a near-zero suspension zeta potential. The changes in settling velocity were accompanied by changes in the diameter and density of the aggregates. At intermediate concentrations, the settling velocity again increased with polyelectrolyte dosage but the major effect of increasing the flocculent nature of the suspension was a corresponding increase in the severity of channelling that occurred within the suspension. The effects of increasing the intensity of pretreatment mixing were limited to a reduction of the suspension settling velocity at low concentrations and a reduction of the severity of channelling that occurred in the more flocculent suspensions. At higher concentrations, the suspension settling velocities were independent of mixing intensity and polyelectrolyte dosage because, at those concentrations, the suspensions settled as an assemblage of discrete particles.

Based on the observations, results, and analyses of this investigation, the following conclusions have been made:

1. Aggregate formation plays a fundamental role in determining the concentration dependent settling velocity of a flocculent suspension at intermediate and higher concentrations in

addition to the role of aggregate formation at low

concentration that has been documented in the literature,

2. Two distinct modes of hindered settling behavior occur in the absence of channelling and solids pressure: "variable interaggregate porosity settling" of aggregates of constant diameter and density occurs at low concentrations; at intermediate concentrations, "constant interaggregate porosity settling" of aggregates whose diameter decreases and density increases with increasing suspension concentration occur,
3. The aggregate diameter and density changes which occur over the constant interaggregate porosity range of settling are systematic and occur in the absence of compression and/or splitting of the aggregates. The relationship between aggregate diameter and density arises because of the basic structure of aggregates and is a function of the primary particle size, density, and flocculent nature, and
4. Because two distinct modes of flocculent hindered settling can occur, none of the currently available settling velocity correlations are applicable over a wide range of suspension concentration. When treated separately, however, the variable and constant interaggregate porosity modes of settling can be readily expressed in terms of suspension concentration with the primary result being that the constant interaggregate porosity settling velocity is proportional to the suspension concentration raised to some negative power.

RECOMMENDATIONS

As previously noted, this investigation was conducted as part of a comprehensive research study on the effects of flocculent nature and pretreatment mixing intensity on the batch- and continuous-thickening behavior of flocculent suspensions. Based on the results of this investigation, the following recommendations have been made regarding project work which is yet to be completed:

1. The variable of pretreatment mixing intensity should be eliminated from further consideration. In future testing, however, only high-intensity mixing should be used to promote a uniform distribution of polyelectrolyte on the primary particles, and because the majority of the data collected at this point has been for high-intensity pretreatment mixing;
2. The sediment tests that were mentioned briefly in this dissertation should be continued to investigate the effects of polyelectrolyte dosage, initial suspension concentration, and initial suspension height on the sediment characteristics, and
3. Pilot-scale, continuous-flow, gravity thickening tests should be conducted with a major goal of comparing the true flux curves of an operating thickener with the flux curves derived from the batch settling data of this investigation. For this to be accomplished, a minimum of four continuous thickening runs should be conducted with each polyelectrolyte dosage of interest. The operational variable of solids loading,

underflow concentration, and underflow withdrawal rate should be such that for each run, a zone of solids whose concentration is independent of depth exists and the zones of constant concentration should represent a wide range of variable and constant interaggregate porosity settling of, for example, 40 kg/m^3 , 80 kg/m^3 , 160 kg/m^3 , and 240 kg/m^3 .

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APPENDIX: EXPERIMENTAL AND CALCULATED DATA

Table A-1. Experimental data and estimated aggregate properties for Celite 512 coated with CatFloc-T at 3.00×10^{-5} g/g and 752 W/m³

Nominal susp'n conc. kg/m ³	Test no.	Mixing time before sampling, min.	Diluted volume of Cat Floc-T, liters	Suspension Zeta potential at 20°C, ζ, mV	Super- natant pH	Measured susp'n conc., C, kg/m ³	Initial settling velocity, V, mm/sec
20	62	2	4	-33.1	8.03	19.6	0.417
30	63	2	4	-30.7	8.10	29.1	0.285
30	83	2	4	-34.4	8.38	29.4	0.280
40	64	2	4	-33.3	8.07	38.5	0.195
50	65	2	4	-35.3	7.98	47.5	0.137
60	66	2	4	-32.8	8.03	57.1	0.096
80	70	2	4	-33.3	7.97	77.5	0.046
100	71	2	4	-33.3	7.93	94.9	0.029
120	72	2	4	-35.1	7.64	115	0.018
150	73	2	4	-39.8	7.78	142	0.010
180	74	2	4	-37.1	7.58	169	0.007
		10	4	-34.3	7.64		

^aVariable interaggregate porosity settling: mean buoyant density = 0.0797 g/cm³, mean diameter = 135 μm.

Estimated aggregate properties				
$(V, \text{mm/sec})^{1/4.65}$	Unhindered settling velocity, $V_o, \text{mm/sec}$	Volume conc. $\phi_a, -$	Buoyant density $(\rho_a - \rho_l), \text{g/cm}^3$	Diameter, $d_a, \mu\text{m}$
0.828	--	--	--	--
0.763	0.830	0.207	0.0754 ^a	142 ^a
--	--	--	--	--
0.704	0.717	0.247	0.0839 ^a	125 ^a
0.652	0.608	0.275	0.0935	110
0.604	0.518	0.304	0.101	97.3
0.516	0.345	0.351	0.119	72.7
0.466	0.200	0.341	0.150	49.1
0.422	0.136	0.352	0.176	37.9
0.374	0.082	0.360	0.213	26.6
0.342	--	--	--	--

Table A-2. Experimental data and estimated aggregate properties for Celite 512 coated with CatFloc-T at 6.25×10^{-5} g/g and 6.42 W/m^3

Nominal susp'n conc. kg/m ³	Test no.	Mixing time before sampling, min.	Diluted volume of Cat Floc-T, liters	Suspension Zeta potential at 20°C, ζ , mV	Super- natant pH	Measured susp'n conc. C, kg/m ³	Initial settling velocity, V, mm/sec
20	2	2	0.5	24.0	8.81	17.4	0.878
30	6	2	0.5	29.4	8.66	25.8	0.600
40	1	2	0.5	28.1	8.37	35.5	0.370
50	27	2	0.5	31.1	8.46	43.1	0.250
60	5	2	0.5	29.9	8.01	52.2	0.145
70	28	2	0.5	32.4	8.15	61.9	0.092
80	3	2	0.5	33.2	7.66	70.2	0.061
100	4	2	0.5	32.9	7.52	89.4	0.033
120	29	2	0.5	32.4	7.67	109	0.020
140	30	2	0.5	30.8	7.56	125	0.013
160	38	2	1	30.8	7.43	149	0.009
180	39	2	1	33.1	7.56	165	0.007
200	40	2	1	34.2	7.42	183	0.006
240	41	2	1	37.3	7.31	217	0.004

^aVariable interaggregate porosity settling: mean buoyant density = 0.0797 g/cm^3 , mean diameter = $135 \mu\text{m}$.

Estimated aggregate properties				
$(V, \text{mm/sec})^{1/4.65}$	Unhindered settling velocity, $V_o, \text{mm/sec}$	Volume conc. $\phi_a, -$	Buoyant density $(\rho_a - \rho_l), \text{g/cm}^3$	Diameter, $d_a, \mu\text{m}$
0.972	--	--	--	--
0.896	1.77	0.206	0.0677 ^a	219 ^a
0.807	1.77	0.284	0.0677 ^a	219 ^a
0.742	1.75	0.342	0.0677 ^a	218 ^a
0.660	1.30	0.377	0.0744	179
0.599	0.928	0.392	0.0849	141
0.547	0.567	0.381	0.0992	102
0.481	0.573	0.365	0.133	61.4
0.429	0.187	0.385	0.153	47.1
0.392	0.099	0.355	0.191	30.7
0.363	0.048	0.302	0.266	18.4
0.349	0.049	0.332	0.267	18.4
0.327	0.034	0.323	0.305	14.3
0.310	--	--	--	--

Table A-3. Experimental data and estimated aggregate properties for Celite 512 coated with CatFloc-T at 6.25×10^{-5} g/g and 752 W/m³

Nominal susp'n conc. kg/m ³	Test no.	Mixing time before sampling, min.	Diluted volume of Cat Floc-T, liters	Suspension Zeta potential at 20°C, ζ, mV	Super- natant pH	Measured susp'n conc. C, kg/m ³	Initial settling velocity, V, mm/sec
20	10	2	0.5	-28.7	8.49	17.7	0.623
30	7	2	0.5	-30.6	--	30.0	0.403
40	8	2	0.5	-30.4	8.28	38.8	0.27
50	9	2	0.5	-29.7	8.20	47.0	0.178
60	11	2	0.5	-30.3	7.77	58.6	0.113
70	12	2	0.5	-31.4	7.73	68.1	0.076
90	31	2	0.5	-31.2	7.72	88.0	0.039
110	32	2	0.5	-31.6	7.73	106	0.024
130	33	2	0.5	-28.5	7.70	122	0.015
160	45	2	1	-33.0	7.49	148	0.009
180	46	2	1	-31.9	7.51	168	0.007
210	47	2	1	-34.6	7.45	184	0.006
240	48	2	1	-35.1	7.34	214	0.004

^aVariable₃ interaggregate porosity setting: mean buoyant density = 0.0720 g/cm³, mean diameter = 183 μm.

Estimated aggregate properties				
$(V, \text{mm/sec})^{1/4.65}$	Unhindered settling velocity, $V_o, \text{mm/sec}$	Volume conc. $\phi_a, -$	Buoyant density $(\rho_a - \rho_l), \text{g/cm}^3$	Diameter, $d_a, \mu\text{m}$
0.903	--	--	--	--
0.823	1.30	0.222	0.725 ^a	181 ^a
0.756	1.35	0.29	0.0715 ^a	185 ^a
0.690	1.030	0.317	0.0801	154
0.626	0.750	0.334	0.0944	121
0.574	0.585	0.356	0.103	102
0.497	0.325	0.366	0.130	67.6
0.450	0.235	0.386	0.148	54.3
0.406	0.146	0.387	0.171	37.9
0.367	0.073	0.355	0.224	24.6
0.342	0.038	0.309	0.293	15.4
0.332	0.028	0.283	0.351	12.3
0.308	--	--	--	--

Table A-4. Experimental data and estimated aggregate properties for Celite 512 coated with CatFloc-T at 2.50×10^{-5} g/g and 752 W/m³

Nominal susp'n conc. kg/m ³	Test no.	Mixing time before sampling, min.	Diluted volume of Cat Floc-T, liters	Suspension Zeta potential at 20°C, ζ, mV	Super- natant pH	Measured susp'n conc. C, kg/m ³	Initial settling velocity, V, mm/sec
20	57	2	4	-24.3	8.22	19.9	1.18
30	58	2	4	-20.0	8.31	30.1	0.807
40	59	2	4	-19.6	8.10	38.7	0.622
50	60	2	4	-17.2	8.10	48.6	0.382
60	61	2	4	-19.7	8.02	57.7	0.260
80	67	2	4	-20.0	7.93	77.9	0.128
100	68	2	4	-26.9	7.85	94.5	0.071
120	69	2	4	-18.7	7.83	113	0.034
150	75	2	4	-22.0	7.64	139	0.014
		10	4	-25.0	7.72		
180	76	2	4	-22.3	7.48	164	0.008
		10	4	-25.6	7.60		

^aVariable interaggregate porosity settling: mean buoyant density = 0.0861 g/cm³, mean diameter μ 216 μ m.

Estimated aggregate properties				
$(V, \text{mm/sec})^{1/4.65}$	Unhindered settling velocity, $V_o, \text{mm/sec}$	Volume conc. $\phi_a, -$	Buoyant density $(\rho_a - \rho_l), \text{g/cm}^3$	Diameter, $d_a, \mu\text{m}$
1.04	--	--	--	--
0.955	1.97	0.176	0.0925 ^a	198 ^a
0.903	2.202	0.236	0.0887 ^a	213 ^a
0.813	2.47	0.328	0.0801 ^a	238 ^a
0.748	--	--	--	--
0.643				
0.567				
0.484				
0.399				
0.351				

Table A-5. Experimental data and estimated aggregate properties
for Celite 512 coated with CatFloc-T at 5.00×10^{-4} g/g and
 6.42 W/m^3

Nominal susp'n conc. kg/m^3	Test no.	Mixing time before sampling, min.	Diluted volume of Cat Floc-T, liters	Suspension Zeta potential at 20°C , ζ , mV	Super- natant pH	Measured susp'n conc. C , kg/m^3	Initial settling velocity, V , mm/sec
20	20	2	0.5	6.0	8.89	16.6	1.47
30	21	2	0.5	5.8	8.52	26.7	1.02
40	22	2	0.5	-1.5	8.45	34.8	0.720
50	23	2	0.5	-2.1	8.30	43.4	0.507
60	24	2	0.5	-4.8	8.18	52.6	0.358
70	25	2	0.5	-7.4	8.00	60.6	0.270
90	26	2	0.5	-7.0	7.63	84.2	0.150
110	36	2	1	-8.9	7.61	107	0.080
130	37	2	1	-11.5	7.55	120	0.032
150	42	2	1	-19.9	7.53	138	0.016
170	43	2	1	-25.5	7.56	157	0.009
190	44	2	1	-25.7	7.56	174	0.007

^aVariable interaggregate porosity settling: mean buoyant density
= 0.0745 g/cm^3 , mean diameter = $266 \mu\text{m}$.

 Estimated aggregate properties

$(V, \text{mm/sec})^{1/4.65}$	Unhindered settling velocity, $V_o, \text{mm/sec}$	Volume conc. $\phi_a, -$	Buoyant density $(\rho_a - \rho_l), \text{g/cm}^3$	Diameter, $d_a, \mu\text{m}$
1.09	--	--	--	--
1.00	2.87	0.198	0.0754^a	264^a
0.932	2.85	0.256	0.0735^a	267^a
0.864	2.17	0.268	0.0878	213
0.802	--	--	--	--
0.755				
0.665				
0.581				
0.475				
0.411				
0.363				
0.342				

Table A-6. Experimental data and estimated aggregate properties for Celite 512 coated with CatFloc-T at 5.00×10^{-4} g/g and 752 W/m³

Nominal susp'n conc. kg/m ³	Test no.	Mixing time before sampling, min.	Diluted volume of Cat Floc-T, liters	Suspension Zeta potential at 20°C, ζ, mV	Super- natant pH	Measured susp'n conc. C, kg/m ³	Initial settling velocity, V, mm/sec
20	13	2	0.5	4.5	8.78	19.6	1.22
30	14	2	0.5	4.2	8.52	28.8	0.865
40	15	2	0.5	2.8	7.95	38.4	0.625
50	16	2	0.5	3.1	7.84	47.8	0.435
60	17	2	0.5	-3.6	7.80	57.3	0.315
70	18	2	0.5	-3.3	7.77	65.6	0.228
90	19	2	0.5	-6.2	7.62	85.6	0.127
110	34	2	1	-9.1	7.71	103	0.073
130	35	2	1	-6.9	7.57	120	0.034
160	49	2	1	-16.2	7.57	146	0.013
190	50	2	1	-17.2	7.61	173	0.007
30	77	2	4	-0.8	8.08	28.8	0.857
		10		-0.3	8.06		
90	78	2	4	1.5	7.84	85.9	0.143
		10		-4.4	7.89		
150	79	2	4	-12.1	7.56	138	0.017
		10		-12.9	7.82		
190	50x		4	-22.0	7.43	171	0.008

^aVariable interaggregate porosity settling: mean buoyant density = 0.0923 g/cm³, mean diameter = 196 μm.

Estimated aggregate properties				
$(V, \text{mm/sec})^{1/4.65}$	Unhindered settling velocity, $V_o, \text{mm/sec}$	Volume conc. $\phi_a, -$	Buoyant density $(\rho_a - \rho_l), \text{g/cm}^3$	Diameter, $d_a, \mu\text{m}$
1.04	--	--	--	--
0.969	2.12	0.178	0.0878 ^a	211 ^a
0.904	2.04	0.224	0.0868 ^a	202 ^a
0.836	1.89	0.270	0.0954 ^a	190 ^a
0.780	1.80	0.310	0.0992 ^a	182 ^a
0.728	--	--	--	--
0.641				
0.570				
0.483				
0.391				
0.347				
0.967				
0.658				
0.416				
0.354				

Table A-7. Experimental data and estimated aggregate properties for Celite 512 coated with CatFloc-T at 1.00×10^{-3} g/g and 752 W/m³

Nominal susp'n conc. kg/m ³	Test no.	Mixing time before sampling, min.	Diluted volume of Cat Floc-T, liters	Suspension Zeta potential at 20°C, ζ , mV	Super- natant pH	Measured susp'n conc. C, kg/m ³	Initial settling velocity, V, mm/sec
20	51	2	1	17.9	8.49	20.2	0.893
30	80	2	4	24.4	8.06	29.4	0.627
		10		22.0	7.98		
40	52	2	1	21.8	8.05	38.8	0.498
60	56	2	4	--	7.80	57.0	0.249
80	53	2	1	24.2	7.91	76.0	0.150
90	81	2	4	23.1	7.86	85.1	0.126
		10		17.9	7.88		
100	54	2	1	3.8	7.89	92.9	0.116
140	55	2	1	--	7.76	130	0.033
150	82	2	4	12.7	7.70	137	0.021
		10		14.6	7.76		

^aVariable interaggregate porosity settling: mean buoyant density = 0.101 g/cm³, mean diameter = 158 μ m.

Estimated aggregate properties				
$(V, \text{mm/sec})^{1/4.65}$	Unhindered settling velocity, $V_o, \text{mm/sec}$	Volume conc. $\phi_a, -$	Buoyant density $(\rho_a - \rho_l), \text{g/cm}^3$	Diameter, $d_a, \mu\text{m}$
0.976	--	--	--	--
0.904	1.48	0.169	0.0941^a	170^a
0.861	1.42	0.199	0.105^a	158^a
0.742	1.25	0.293	0.105^a	147^a
0.665	--	--	--	--
0.640				
0.629				
0.482				
0.435				

Table A-8. Settling velocity data for batch tests conducted with initial suspension height of 60 cm and pretreatment mixing intensity of 6.42 W/m^3

Nominal Suspension concentration, kg/m^3	Test number	Polyelectrolyte dosage P/DE, g/g	Measured suspension concentration $C, \text{kg/m}^3$	Settling velocity, $V, \text{mm/sec}$
70	S-2	5.00×10^{-4}	64.9	0.262
90	S-1	5.00×10^{-4}	88.5	0.134
130	S-3	5.00×10^{-4}	125	0.031
70	S-6	6.25×10^{-5}	64.1	0.102
90	S-5	6.25×10^{-5}	81.6	0.050
130	S-4	6.25×10^{-5}	125	0.0016